SODIUM TECHNOLOGY QUARTERLY REPORT
January—March 1971

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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SODIUM TECHNOLOGY QUARTERLY REPORT

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FOREWORD

The Sodium Technology Quarterly Report describes the current activities of the Sodium Technology Program at Argonne National Laboratory, sponsored by the Coolant Chemistry Branch of the USAEC Division of Reactor Development and Technology. In the areas of sampling and analysis and on-line monitoring of impurity elements, Argonne is involved in research and development activities as well as in the coordination of national efforts to meet the near-term needs of sodium technology, particularly those of FFTF. Argonne's program also includes research and development work on fission-product behavior and control, sodium chemistry, and materials-coolant compatibility. The program is a coordinated effort between two Argonne Divisions--Chemical Engineering and Materials Science.

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ABSTRACT

The research, development, and management efforts of Argonne
National Laboratory's Sodium Technology Program for the period
January–March 1971 comprised activities in the following areas:
(1) In the national meter program, coordination of the national
effort to produce a standardized on-line oxygen meter continued;
other work included development of on-line meters for carbon and
hydrogen, development of a steam-generator leak detector, and
design and testing of meter modules for FFTF. (2) In the
analytical standards program, work has begun on the preparation
of RDT standards relating to purity specifications for sodium
and cover gas; laboratory studies involved development and testing
of interim methods of sampling and analysis. (3) Investigation
of methods for detection and characterization of fuel-cladding
failures proceeded with the development of a method for detecting
^{135}I in reactor sodium by separation and counting of its daughter
^{135m}Xe. (4) Studies of the chemistry of liquid sodium were
directed toward investigation of the $Na-Na_2O-NaOH-NaH$ phase
diagram and examination of the vacuum distillation method as
a means of determining oxygen and carbon in sodium. (5) Studies
were continued on the transport of carbon in sodium-steel systems
and on the development of methods for determining activities of
oxygen and carbon in sodium by equilibration of metal specimens.

SUMMARY

On-Line Impurity Monitors

A national program has been instituted for developing, testing, and
establishing commercial availability of meters for the sodium systems of
FFTF and LMFBRs. Argonne is coordinating the national program as well
as participating in it. In this program, meters for oxygen, carbon, and
hydrogen and a leak detector for steam generators are being developed
and characterized. Meter modules that provide flow and temperature con-
trol are being developed for FFTF; these modules will be tested at EBR-II.

Recently, the Advisory Group of the National Meter Program met to
review the progress made in the program and to establish plans for field-
testing standardized on-line impurity meters during FY 1972. At another
meeting, the expected needs of the LMFBR program for meters and modules
were described to potential manufacturers, and purchase specifications
were discussed. All the manufacturers participating in the meeting indi-
cated considerable interest in becoming suppliers for the meters, com-
ponents, or modules.

Oxygen Meter Development. A program has been established that is
expected to result in the commercial availability of improved electro-
chemical oxygen meters by early FY 1972. ANL is coordinating efforts at

WADCO and the Zirconium Company of America (Zircoa) to produce improved solid electrolyte tubes (isostatically pressed thoria-7.5 wt % yttria) for the meters and is also coordinating efforts at Westinghouse and Brookhaven National Laboratory to evaluate the material by performance tests in sodium. Two cells with electrolyte tubes produced at WADCO were operated for more than 2000 hr at 370 to 485°C prior to failure. Most of the test time was at the higher temperature. Longer life is expected at the lower operating temperature of 370°C, which has been selected for the oxygen-meter characterization program.

A Westinghouse gas-reference oxygen meter with a WADCO electrolyte tube was installed and operated up to 425°C in the sodium loop of the Oxygen Meter Calibration Apparatus (OMCA). A total of ∿1350 hr of satisfactory operation was accumulated prior to a scheduled shutdown. These tests showed that the high-purity electrolyte material produced at WADCO is more resistant to attack by sodium and gives better electrical performance at the low oxygen levels typical of reactor sodium systems than previously available materials. Preliminary information on tube life in sodium is encouraging.

Zircoa has produced 20 electrolyte tubes using the WADCO process specifications. These are en route to WADCO and Westinghouse for evaluation. An additional 180 tubes are to be produced subject to WADCO approval. Twelve Zircoa tubes from five batches will be incorporated into oxygen meters at Westinghouse, and these will be used for meter-characterization tests at ANL.

The performance of ten of these standard meters having two electrolyte tubes from each of the five batches will be determined over an extended period of time. (A matching set of ten meters having electrolytes from the same Zircoa sintering batches will be tested at WARD.) In the ANL tests, the ten meters will be connected in series with a specimen-equilibration module, which will be used to calibrate the oxygen meters by the vanadium-wire equilibration method, and with a cold trap to control the oxygen content of the sodium. Construction of the module and the supporting sodium system is in progress and is expected to be completed by the time the meters are received.

Hydrogen Meter Development. Development work is being continued on a hydrogen-activity meter having a direct pressure readout of the equilibrium hydrogen pressure above the sodium. The sensitivity of the meter was tested by adjusting the cold-trap temperature between 110 and 190°C and measuring the apparent solubility of hydrogen in the sodium with the meter. The data obtained were self-consistent and extend available data down to a concentration of 0.03 ppm hydrogen in sodium.

An evaluation was made of the potential hydrogen losses on removing reactor cover-gas samples through a vapor trap. This evaluation indicated that <1% of the hydrogen content of the gas would be lost if equilibrium were maintained between the gas and the condensed sodium during the cooling process.

Carbon Meter Development. The goal of this work is a commercially available on-line carbon meter that will indicate the probability of significant carbon transfer taking place in R & D and LMFBR systems. Present work is directed toward the testing and improvement of the United Nuclear Corporation (UNC) diffusion meter, which measures the rate of diffusion of carbon through an iron membrane. Two diffusion-type carbon meters are being operated in a flowing sodium system (Test and Evaluation Apparatus, TEA): one is a UNC meter with a stainless steel housing; the other is an ANL modification, which has a molybdenum liner in the high-temperature housing.

Improved operation of both carbon meters has resulted from revisions in the carbon detection systems; these revisions allow instrumental compensation for trace carbonaceous impurities in the decarburizing gas. Measurements taken over a one-month period, during which time no significant change was made in the carbon content of the sodium in the TEA, showed that both meters gave carbon flux readings of 0.001 $\mu g/(cm^2)(min)$ ±25%. When a Fe-5% C alloy was added to the high-temperature test section (630°C), the carbon flux increased and remained constant at the higher level until the temperature of the test section was lowered.

The effects of system variables on the responses of the meters were also investigated. These included separately increasing the cold-trap temperature, the loop temperature, and the primary sodium flow rate. Only transient increases in the carbon fluxes were obtained in all three instances. Some of these were large increases (as much as 1000%) that lasted for several hours. During these tests, the responses of the two meters differed. These observations suggest that the transients may have been caused by carbon-containing particulate being carried past the carbon meters.

Meter Modules for FFTF. The objective of this work is to design, prooftest, and establish commercial availability for on-line meter modules to be installed at FFTF. These modules include flow and temperature controls as well as the meters for monitoring impurities.

Fabrication of two oxygen-hydrogen meter modules and electrical consoles was completed. Final assembly and check-out of the modules and consoles is under way. One unit will be tested at ANL; the other will be installed at EBR-II on the Radioactive Sodium Chemistry Loop (RSCL) in Cell B. The data package for installation and testing of the oxygen-hydrogen meter module at EBR-II has been prepared and has received EBR-II management approval, and installation has been started.

The data package for installation and testing of the specimen equilibration-carbon meter module in Cell C of the RSCL at EBR-II has been completed and sent to EBR-II for review and approval.

Detection of Leaks in Steam Generators. ANL is supplying a hydrogen-meter leak detector to the Liquid Metal Engineering Center (LMEC) where it will be used on the Sodium Components Test Installation. Fabrication of this leak detector was completed and the unit was shipped to LMEC. The document submittal requirements of LMEC were satisfied, and an operating manual was written. Completion of the instrument package is awaiting delivery of some of the components.

Design of a preliminary model of a leak detector for LMFBR steam generators has been completed and fabrication has been started. This model will be tested on an available sodium loop. Detailed designs of the system will be provided to EBR-II for use in instrumenting their steam generator plant with water-to-sodium leak detectors. Linear actuators are being considered for use as sodium pumps on this system; two of these units are being procured for testing.

Characterization of Impurity Meters and Meter Response to Impurity Species. The primary goal of this work is the determination and interpretation of nonmetallic impurity levels in cold-trapped sodium as a function of cold-trap operating parameters and procedures. The methods for determining the impurities (O, C, H, and N) in the sodium will be on-line impurity monitoring, and sampling and analysis. Experimental work will be carried on in a pumped-sodium apparatus (Apparatus for Monitoring and Purifying Sodium, AMPS) that will provide stable but adjustable impurity levels in the sodium fed to the test cold trap.

The piping and equipment layouts and the piping stress-analysis calculations for AMPS have been completed. Work is in progress on the detailed design of components, instrumentation and control systems, electrical systems, and the component fabrication packages. Construction of AMPS is scheduled to start in July 1971.

Analytical Standards Program

Administrative Activities. Preliminary purity specifications for sodium and cover gas systems have been generated and published in a document entitled "Interim Purity Specifications for Large Operating Sodium Systems." These specifications are being used as a basis for revising two RDT standards and generating a third standard. The first revision of "Reactor Grade Sodium--Purchase Specifications" is nearly complete, and the first revision of "Sodium Cover Gas" has been started. A proposal describing the scope of and the need for a new RDT standard entitled "Purity Specifications for Large Operating Sodium Systems" has been sent to the RDT Standards Office at LMEC.

An examination of the analytical and chemical problems associated with the use of tetraboron carbide (B_4C) control rods in FFTF has been made. The findings were as follows: (1) Preliminary evidence obtained at WADCO indicates that B_4C will probably be stable toward 500°C sodium in a fast flux. (2) Available literature data indicate that, in the presence of sodium at 800°C, B_4C does not interact appreciably with Types 304 and 316 stainless steel. (3) Detection and location of failure in B_4C control rods will best be accomplished using radium (radon) tags for detection and xenon tags for location. (4) Tritium production via the reaction $^{10}B(n,2\alpha)T$ will be significant. (5) The helium produced by (n,α) reactions on B_4C, if released suddenly, could cause gas blanketing problems similar to those that can occur with driver fuel.

Laboratory Activities. A set of experiments to determine the effect of line length on the oxygen content of sodium has been completed. In these experiments a sodium change in the oxygen content of sodium at 350°C

was produced at one end of a 100-ft-long section of Type 304 stainless steel tubing, equipped with an oxygen meter at each end. The magnitude of the change in concentration at each end of the section was measured, as well as the time required for detection of the change. The results indicate that no significant loss in accuracy results from passing the sodium through 100 ft of tubing and that the meter response to a change is limited only by the time required for the sodium to travel through the tubing.

A filter assembly for collecting particulates from large sodium systems has been designed and two assemblies have been constructed. One of these is being tested at ANL-Illinois to verify that design characteristics, such as flow rate and pressure drop, have been met; the other will be used to collect particulates from EBR-II sodium.

A commercially available carbon analyzer has been modified to increase its sensitivity for determining the carbon content of iron wires. The modifications involve (a) converting the carbon dioxide (the compound normally produced by this analyzer) to methane, (b) measuring the methane with a flame-ionization detector, and (c) lowering the blank by decarburizing the iron accelerator used in the procedure.

Initial experiments with a high-temperature gas chromatographic separation of sodium vapor from the permanent gases indicate that, in the temperature range between 400 and 650°C, sodium vapor is retained on a column while the permanent gases pass through.

Fission Product and Cover Gas Technology

Failed Element Detection and Location.

A possible method for locating fuel failures in LMFBR systems after reactor shutdown involves intermittent restriction and release of sodium flow through selected fuel assemblies. In this concept, restriction of flow through a particular assembly would cause a pressure rise in the sodium coolant and force it into cladding defects. Removal of flow restriction would result in a reduction of coolant pressure and release of fission products (as fission gases or as solutes in sodium) from defective fuel elements in the assembly being tested; released fission products would be detected by a suitable monitoring system. This technique may also give diagnostic information since only plenum gas would be released from fuel with defects at the top of the cladding, and fission products (such as iodine) leached from the fuel by contact with sodium would be released from cladding defects existing below the plenum zone.

An assessment was made of problems associated with characterizing fuel-element failures in which there is a simultaneous release of fission gas and sodium from the fuel (burst failures). The sequence of events leading to a burst failure would be as follows: (1) development of a leak early in fuel life, (2) entrance of sodium into the fuel element, (3) compression of plenum gas, and finally (4) a sudden cladding failure below the sodium level (possibly resulting from sodium-fuel reaction). If cover-gas analysis for ^{135m}Xe is the only diagnostic method used, ~1 hr might be required to determine whether the activity measured is from this type of failure. Moreover, accurate detection of sodium-fuel contact by cover-gas analysis would probably be impossible if other elements that intermittently leak only gas are present in the reactor.

Development of Radioisotope-Monitoring Methods. The method presently being developed for monitoring ^{135}I in reactor sodium involves the separation and assay of its daughter ^{135m}Xe. In this connection, information is needed on the kinetics of removal of xenon from liquid sodium. By the use of calculated diffusion coefficients, estimates have been made of transfer times for xenon removal in gas-liquid contactors. For a gas-bubbler sparger of the type being built for testing the iodine-monitoring method, the estimates indicate that 99% of the xenon will be removed from sodium at 500°C in about 3 min of sparging at 1000 cm^3/min. Similar calculations for a spray-tower contactor indicate a shorter removal time (99% removal from 0.1-cm-dia drops in ⌄8 sec); however, the gas-bubbler sparger has the advantage of inherent simplicity of design.

Design of the gas-bubbler sparger has been completed and construction has been started. Installation of the sparger in a sodium test facility is presently scheduled for June 1971.

Sodium Chemistry

The Sodium-Sodium Oxide-Sodium Hydroxide-Sodium Hydride System. This program seeks an understanding of the behavior of oxygen- and hydrogen-bearing species in liquid sodium. Elucidation of the phase relations of the Na-rich corner of the Na-O-H ternary system is part of this program. In this connection, a working diagram of the Na-Na$_2$O-NaOH-NaH system, constructed earlier, has been updated to make it consistent with new X-ray findings.

Vacuum Distillation as an Analytical Method for Impurities in Sodium. A study has been initiated to characterize the impurity reactions that may occur in the evaporation-concentration step of distillation analyses for oxygen, carbon, and nitrogen in sodium and to determine whether or not such reactions lead to significant errors in analyses for nonmetallic elements in sodium. A still with a 1-kg capacity has been designed and fabricated and is now being assembled.

Materials-Coolant Compatibility

Studies of Carbon Transport in Sodium-Steel Systems. The objectives of this work are (1) to obtain an understanding of the thermodynamics and kinetics of carburization-decarburization processes involving austenitic and ferritic steels and (2) to correlate compositional and microstructural changes with mechanical-property behavior of these materials.

Additional experiments to determine the distribution of carbon between sodium and iron and iron-base alloys at 650 and 750°C have been conducted. The carbon analyses of the equilibrated foil specimens of Types 304 and 316 stainless steel and the sodium samples indicated a substantial increase in the carbon concentrations when a carbon source was present in the loop. Carbon contents of the sodium have ranged between ⌄0.4 and 25 ppm in the experiments to date, whereas the steels contained between ⌄0.1 and 1.3 wt % carbon at these temperatures. Further experiments to determine the distribution of carbon between these alloys and liquid sodium are in progress.

Determination of Nonmetallic Impurities in Sodium by the Equilibration Method. The purpose of this work is to develop methods for accurately measuring the activities of nonmetallic elements, e.g., O, C, N, and H, in sodium at the low concentrations of interest for LMFBR applications.

The method for determining oxygen activity in liquid sodium involves equilibration of vanadium wires in sodium at 750°C for 4 hr and subsequent measurement of the oxygen content of the vanadium. Recent tests of the method, in which vanadium wires were exposed, under standard conditions, to liquid sodium of known oxygen concentrations, have resulted in slightly revised values for the distribution coefficients. The recent data are considered more reliable than previous data and are being used to establish the precision of the method.

Experiments have also been performed to investigate the effects of the nonmetallic impurities carbon, nitrogen, and hydrogen on the oxygen measurement by this method. The results indicate there is no measurable effect of either carbon or nitrogen on the oxygen measurement under conditions in which (1) carbon concentrations in sodium are higher than can reasonably be expected in reactor systems and (2) nitrogen concentrations in vanadium are in a range (i.e., <1000 ppm) typical of the purity of the vanadium wire used in the oxygen-activity measurements. Experiments to determine the effect of hydrogen in sodium on the oxygen activity determined by this method are in progress.

A UNC electrochemical oxygen meter operating at 352°C has been calibrated using the standard vanadium-wire equilibration method over the range 0.3 to 15 ppm oxygen in sodium. All of the data points were within 1 mV of the curve, as was found for another UNC cell calibrated in this manner.

The operating characteristics of a modified UNC oxygen meter, in which the Cu, Cu_2O reference electrode was replaced by Na, Na_2O, have been determined. The similarity in the behavior of this cell and a UNC oxygen meter (Cu, Cu_2O reference electrode) operating on the same apparatus suggests that deviations from theoretical predictions result from problems associated with impurities in the thoria-15 wt % yttria electrolyte rather than the reference electrodes.

The equilibration method is being extended to the measurement of carbon activities in sodium. Specimens of the candidate detector metals, vanadium and iron, have been exposed to flowing sodium at 750°C with a carbon source present in the loop. The carbon content of the vanadium could be qualitatively correlated with the carbon content of the sodium samples; however, the carbon concentrations of iron were erratic and yielded values in the range of 20 to 30 ppm. Possible problems related to the use of iron as a detector are as follows: (1) reequilibration of the iron specimens during cooling, (2) pickup of additional surface carbon as a result of chromium mass transfer, deposition, and conversion to a surface carbide, and (3) the internal carburization of carbide-forming impurity elements in the iron at the low carbon activities that exist in the sodium. Experiments to examine these possibilities are planned.

I. ON-LINE IMPURITY MONITORS
(J. T. Holmes)

Argonne National Laboratory (ANL) is coordinating, as well as participating in, a national program for developing, testing, and establishing commercial availability of meters for use in FFTF and in other LMFBR systems. The meters to be developed and characterized in this program are monitors for oxygen, carbon, and hydrogen impurities in sodium and a leak detector for steam generators. Meter modules that provide flow and temperature control are being developed for FFTF. These modules will be tested at EBR-II.

On January 27, 1971, the Advisory Group of the National Meter Program met to review recent progress and to establish plans for field-testing standardized on-line impurity meters during FY 1972. On January 28, 1971, the expected needs of the LMFBR program for meters and modules were described to potential manufacturers, and purchase specifications were discussed. All the manufacturers participating in the meeting indicated considerable interest in becoming suppliers of the meters, components, or modules.

A. Oxygen Meter Development (V. M. Kolba, J. M. McKee, L. J. Marek)

1. Electrolyte Development

ANL is coordinating the joint efforts of WADCO, the Zirconium Company of America (Zircoa), Brookhaven National Laboratory (BNL), and Westinghouse to standardize an improved version of the electrochemical oxygen meter, which utilizes an improved solid electrolyte tube (isostatically pressed thoria-7.5 wt % yttria) and a gas reference electrode. Recent work by the various contractors in the electrolyte-development program is described below.

Thirty-one high-purity electrolyte tubes have been produced at WADCO by the isostatic pressing procedure. The disposition of these tubes and progress in characterizing them are summarized in Table I-1. The results of the tests continue to indicate that improved cell performance can be expected from the high-purity electrolyte material. Tube life at 370°C, the expected operating temperature, remains to be established.

At the end of March 1971, Zircoa had produced the first 20 (of an order for 200) electrolyte tubes using the WADCO process specifications and powder that had been checked by WADCO for purity and compacting properties. Eight of these tubes will be characterized and performance-tested at WADCO and Westinghouse. Some of the other 12 tubes will be incorporated in Westinghouse oxygen meters of the type to be used in FFTF and sent to ANL. Production by Zircoa of the remaining 180 tubes will be contingent on the satisfactory performance of samples from the first 20.

TABLE I-1. Utilization of Electrolyte Tubes Produced at WADCO by Isostatic Pressing

Contractor	No. of Tubes	Use	Results
Brookhaven National Laboratory (BNL)	5	Calibration of cells in stirred sodium pots by the uranium-tab method, using $Na-Na_2O$ reference electrodes. Direct comparison with other electrolyte compositions isopressed at GE Research Labs.	Better electrical performance of WADCO tubes than commercial purity tubes, particularly below 10 ppm O in Na. Tentative preference for 7.5 over 15 wt % yttria content. $Na-Na_2O$ reference electrode not recommended for power-plant meters. 370°C minimum temperature for consistent electrolyte performance.
Westinghouse Research Laboratories (WRL)	(14)	Platinum-gas reference electrode installed in 14 tubes. 5 sent to WARD, 6 sent to ANL in W̲ meters (model 2), 1 held for ANL, 2 reserved for tests at WRL.	
	2	Electrical performance tests in sodium pots. Electrolyte surfaces examined with scanning electron microscope and microprobe analyzer after screening tests and sodium exposure (tubes tested at WADCO also examined).	Better electrical performance than commercial purity tubes. Correlation between impurity concentrations at grain boundaries and attack by sodium and phosphoric acid. (No second-phase material or etching of grain-boundary triple points by phosphoric acid on WADCO tube samples.)
Westinghouse Advanced Reactors Div. (WARD)	5	5 tested in W̲ meters (model 2) in pumped sodium loops.	Tube 42-1-B operated 2591 hr, including 1577 at 510°C. Tube 42-2-B operated 2059 hr, including 1760 at 510°C. Both failed by short circuit without prior loss of performance. Tube 49-2-3 failed at 91 hr due to operator error. Tube 73-1-3 operated 249 hr at ∿370°C. Suspect mechanical flaw caused early failure. Tube 42-2-D operated 1011 hr at ∿370°C. Indication that 1 ppm hydrogen will not significantly affect the oxygen activity in sodium heat-transfer system.
Argonne National Laboratory (ANL)	13	3 W̲ meters (model 2) sent to EBR-II, 3 installed at ANL-Illinois. 7 tubes held for laboratory use (1 at WRL).	1 meter tested for ∿1350 hr in OMCA (details in text, this section). Meter remains in operating condition.
WADCO Corp.	6	Subjected to sodium compatibility tests, destructive examination and analysis.	Basis for selection of fabrication process specifications. Resistance of high-purity material to attack by sodium confirmed.

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2. Test of Westinghouse Oxygen Meters

During this period, six Westinghouse (W) gas-reference oxygen meters with electrolyte tubes fabricated by WADCO were received by ANL. One of these meters was incorporated into an assembly for radiation testing at EBR-II,[1] and four were incorporated into the two oxygen-hydrogen meter modules now being fabricated (see Section I.D.). The sixth meter was installed on a small pumped-sodium apparatus. The disposition of these meters and the electrolyte identification numbers are given in Table I-2.

The apparatus being used to test meter E6 (Oxygen Meter Calibration Apparatus, OMCA), provides for testing up to four oxygen meters and for determining their stability as a function of operating life in a sodium system having sodium flow rates up to 0.5 gpm at temperatures up to 485°C. A cold trap is provided in this system for controlling the oxygen level. The meter on the OMCA was put into operation late in January 1971 and was operated successfully for ∿1350 hr at temperatures between 370 and 425°C. Most of the test time was at the higher temperature. OMCA was then shut down to devote more effort temporarily to the meter modules for EBR-II (Section I.D.).

During this test the temperature coefficient of the cell and the cell response to changes in oxygen level were measured. Temperature-coefficient tests were conducted in the temperature range 312-400°C and at various oxygen levels in the sodium (oxygen levels determined from the cold-trap temperatures). The temperature coefficient of the meter, using air in the reference electrode, was found to be positive and small, being of the order of 0.06 mV/°C. The emf data at three oxygen levels are shown in Table I-3.

Our data on cell emf versus oxygen content of sodium at 400°C, along with averaged data from two meters tested by Westinghouse (WARD) at 370°C, are shown in Fig. I-1. Also shown in the figure are theoretical curves based on the solubility data of Eichelberger[2] at 370°C and that of Smith and Kassner[3] at 400°C. The WADCO electrolyte tubes used in the tests differed as to powder batch and sintering batch (Westinghouse tests used tubes 42-1-B and 42-2-B, whereas the ANL meter used tube 49-1-4); these differences may account for the observed differences in responses of the meters.

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[1] This assembly was shipped to EBR-II early in February 1971. However, the forthcoming installation of the oxygen-hydrogen meter module at EBR-II (see Section I.D.) has obviated the need for this preliminary test. The oxygen meter will be used as a spare assembly for the meter module.

[2] R. L. Eichelberger, AI-AEC-12685 (1968).

[3] D. L. Smith and T. F. Kassner, Corrosion by Liquid Metals, pp. 137-149, Plenum Press, New York (1970).

TABLE I-2. Utilization of Westinghouse Oxygen Meters at ANL

Meter Designation	WADCO Electrolyte Designation	Use
E1	72-2-2	O-H meter module to be tested at
E2	73-1-2	ANL Illinois
E3	49-1-1	O-H meter module to be tested on
E4	49-1-2	RSCL at EBR-II
E5	49-1-3	Radiation test at EBR-II[a]
E6	49-1-4	OMCA test

[a]Now a spare assembly for RSCL meter module (see text).

TABLE I-3. Temperature-Coefficient Data for Oxygen Meter Tested on OMCA

Oxygen Conc., ppm	Initial Temp., °C	Final Temp., °C	Initial Emf, V	Final Emf, V	Temp. Coeff., mV/°C
1	400	312	1.746_9	1.741_8	0.058
2.1	400	330	1.732_9	1.729_7	0.046
5.8	400	328	1.712_9	1.708_4	0.062
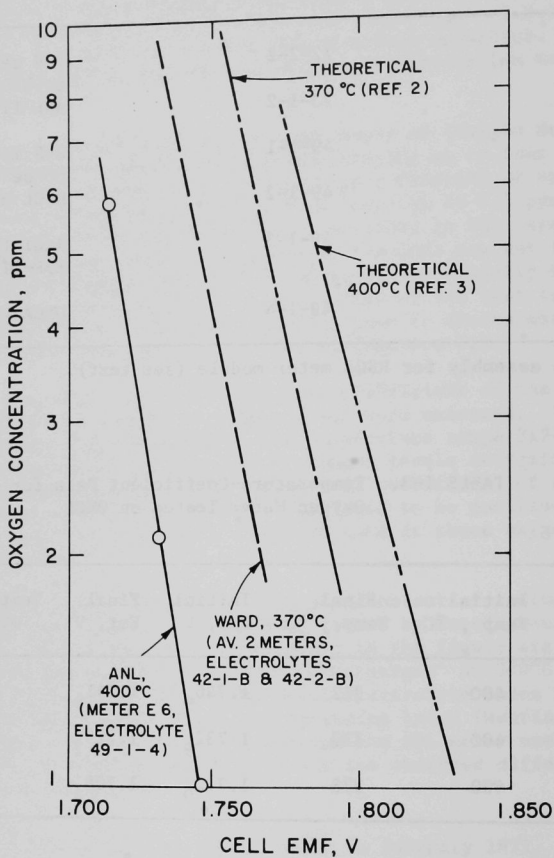
Fig. I-1. Comparison of Westinghouse Oxygen
Meters Tested at ANL and WARD

3. Oxygen-Meter Characterization Program

To provide a statistically significant measure of the calibration stability of the oxygen meter, 20 FFTF-type meters will be tested: 10 at ANL and 10 at Westinghouse (WARD). Each set of ten meters has two electrolyte tubes from each of five batches. Initial calibration curves at oxygen levels from <1 to 15 ppm will be determined for all meters at 370°C by the vanadium-wire equilibration method, which measures the oxygen activity in sodium. These calibrations will be repeated after three months of continuous operation at 370°C to determine calibration stability. The temperature coefficients of the meters will be measured at intervals during this period. Testing will continue for at least a year, under conditions determined by results during the first three months.

For the ANL tests, the ten meters will be connected in series with the laboratory prototype specimen-equilibration module and with a cold trap used to control the oxygen content of the sodium. Construction of the loop and the module is in progress, and the meters are being produced by Westinghouse. It now appears that the meters will not be delivered to ANL until June or July 1971, as a result of delayed receipt of high-purity tubes from Zircoa. The characterization program will start as soon as the meters are installed.

B. Hydrogen Meter Development (D. R. Vissers, L. G. Bartholme)

The goals of this program are the design, development, and proof-testing of an on-line hydrogen meter for measuring the hydrogen activity in primary and secondary LMFBR sodium systems. The meter being developed at ANL is a diffusion-type hydrogen-activity meter (see ANL/ST-2, p. 1-10). Appropriate response-test procedures and on-line calibration requirements for the meter are being evaluated.

Problems attending the operation of the hydrogen meter in the equilibrium mode for long periods of time and at low levels of hydrogen in the sodium have necessitated a revision in the operating procedure. The hydrogen meter can be operated in two modes. The first is in equilibrium mode in which the equilibrium hydrogen pressure above the sodium is measured directly and then related to hydrogen concentration in the sodium by Sieverts' law; the second is a dynamic mode, in which the hydrogen flux across the membrane is monitored by an ion pump. The operation of the meter in the equilibrium mode permits the determination of the hydrogen activity of the sodium directly. However, during continuous operation in this mode for long periods of time, especially at low levels of hydrogen (<0.3 ppm), degassing from the high-vacuum components creates an error in the measurement. One method of avoiding this problem is to use the dynamic mode as the normal mode of operation, with the equilibrium mode being used only intermittently. Operation in the equilibrium mode will provide a calibration for the dynamic mode of operation. Methods of reducing degassing are also being investigated.

1. **Sodium Analytical Loop (SAL) Studies**

During recent studies on SAL, the sensitivity of the hydrogen activity meter was tested during operation in the equilibrium mode. The sodium was first cold-trapped stepwise to 110°C, and the apparent hydrogen solubility[4] of the sodium measured at the various cold-trap temperatures. The results of these preliminary studies are shown in Fig. I-2. Although the meter did not reach equilibrium values that were completely stable at the cold-trap temperatures tested, the responses are believed to be adequate at these low levels.

It should be noted that these hydrogen solubility values are slightly higher than those reported earlier (ANL/ST-3, p. 1-8). The earlier values were obtained from dynamic-mode measurements, in which the calibration of the ion pump (i.e., determination of the relationship between the ion-pump current and the hydrogen level of the sodium) was accomplished at a single hydrogen level. It is now clear that a single-point calibration of the ion-pump current is not adequate for accurate hydrogen-meter operation in the dynamic mode, probably because of changes in the pumping speed of the ion pump.[5]

2. **Feasibility of Sampling Cover Gas for Hydrogen Through a Vapor Trap**

A calculational study was carried out to determine the feasibility of sampling cover gas through a vapor trap without significant hydrogen loss.

The hydrogen content of the cover gas of a liquid sodium system, in which the cover gas and sodium are in equilibrium, will be fixed by the hydrogen activity of the sodium. The ability to analyze the hydrogen content of the cover gas by standard gas-chromatographic procedures is complicated by the fact that as the cover gas (which contains sodium vapor and aerosol) is cooled to near room temperature, liquid sodium, sodium hydride, and, finally, solid sodium are formed.

The possibility was considered of preventing the formation of large quantities of sodium hydride, and consequently the loss of large amounts of hydrogen from the cover gas, during cover-gas cool-down by cooling the cover gas in a controlled manner. The cool-down process must remove the sodium aerosol and condense the sodium vapor while maintaining equilibrium between the condensed and vapor phases. It was found that if the cover gas is cooled in this manner, only a small fraction of the total hydrogen in the cover gas will be removed from the cover-gas sample.

For example, consider a sodium system at 450°C which contains 0.88 ppm of dissolved hydrogen, an amount sufficient for saturation of the sodium at 200°C. The cover gas in equilibrium with this system will

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[4] The assumption is made that the solubility of hydrogen in sodium obeys Sieverts' law, even at these low hydrogen levels.

[5] J. H. Singleton, "Hydrogen Pumping Speed of Sputter-Ion Pumps," J. Vac. Sci. Technol. 6(2), 316-321 (1969).
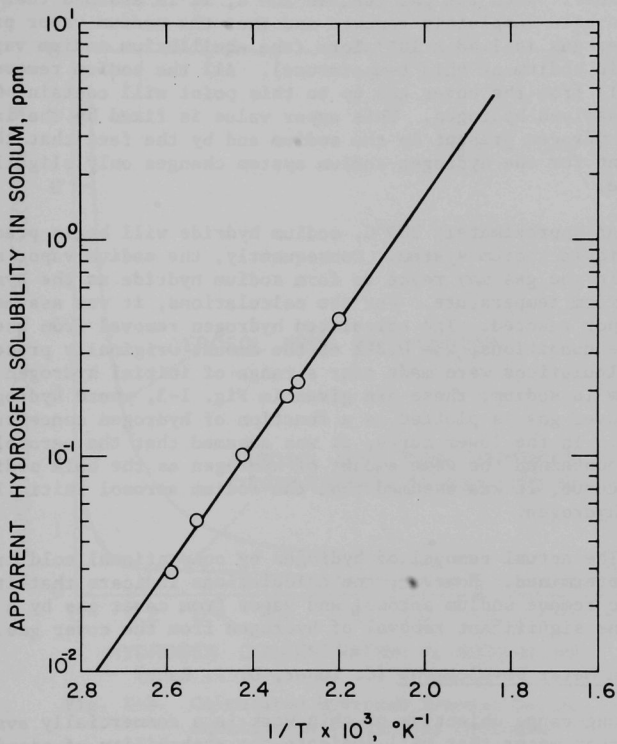
Fig. I-2. Apparent Solubility of Hydrogen in Sodium
as Determined by Hydrogen-Activity Meter

contain sodium vapor (1.3 Torr) and some aerosol, which for this example was assumed to be equivalent to 13 Torr of sodium vapor pressure. This aserosol is assumed to contain the same concentration of hydrogen as the bulk sodium (0.88 ppm). The hydrogen vapor pressure in the cover gas that is in equilibrium with this sodium is about 3.61×10^{-2} Torr. A sample of this cover gas is removed from above the sodium and cooled in a controlled manner. When the gas reaches 200°C, it is assumed that the aerosol has been completely removed and that the sodium vapor pressure in the cover gas is 1.48×10^{-4} Torr (the equilibrium sodium vapor pressure above liquid sodium at this temperature). All the sodium removed (vapor and aerosol) from the cover gas up to this point will contain ~ 0.88 ppm or less of dissolved hydrogen. This upper value is fixed by the initial amount of hydrogen present in the sodium and by the fact that the Sieverts' law constant for the hydrogen-sodium system changes only slightly with temperature.

At approximately 200°C, sodium hydride will begin precipitating from the liquid sodium system. Consequently, the sodium vapor still remaining in the gas may react to form sodium hydride as the system is cooled to room temperature. For the calculations, it was assumed that all the vapor reacted. The calculated hydrogen removal from the gas, under these conditions, was 0.24% of the amount originally present. Similar calculations were made over a range of initial hydrogen concentrations in sodium; these are given in Fig. I-3, where hydrogen removal from the cover gas is plotted as a function of hydrogen concentration in the sodium. In the lower curve, it was assumed that the aerosol in the cover gas contained the same amount of hydrogen as the bulk sodium; in the upper curve, it was assumed that the sodium aerosol initially contained no hydrogen.

The actual removal of hydrogen by conventional cold traps has not been determined. However, the calculations indicate that it may be possible to remove sodium aerosol and vapor from cover gas by a vapor trap with no significant removal of hydrogen from the cover gas.

C.   Carbon Meter Development (C. Luner, D. J. Raue)

The long-range objective of this work is a commercially available on-line carbon meter that will indicate the probability of significant carbon transfer taking place in R & D and LMFBR systems.   The more immediate objectives are the testing and improvement of the UNC diffusion-type carbon meter, which will be incorporated into a prototype module containing the necessary flow and temperature control devices (Section I.D.).

Recent work has been directed toward improving the reliability of the carbon meter and determining the responses of the UNC probe (stainless steel housing) and an ANL-modified probe with a molybdenum-lined housing (see ANL/ST-8, p. 17) to increases in cold trap and loop temperatures and to additions of carbon. The two probes are being tested on a pumped-sodium system, the Test and Evaluation Apparatus (TEA).
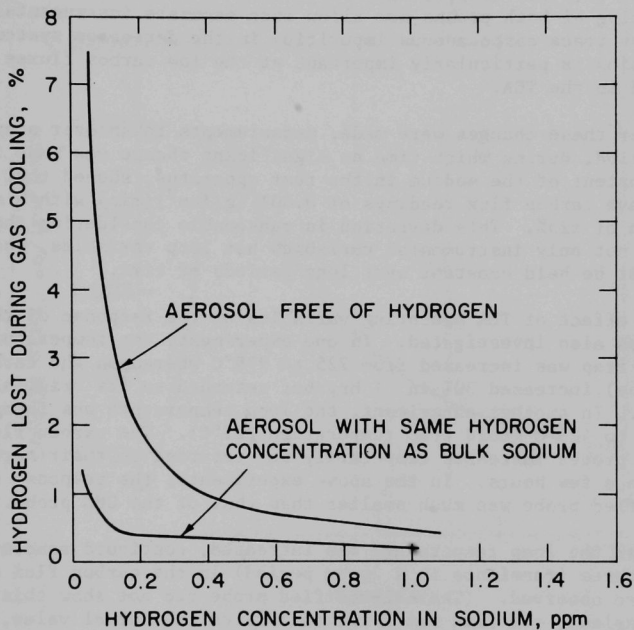
Fig. I-3. Calculated Hydrogen Removal During
Equilibrium Cooling of Hydrogen-
Sodium Gas Systems from 450°C
(P_{Na} assumed to be 13 Torr)

During past operation of the two probes, it had been observed
that the carbon flux of the UNC probe was about a factor of three higher
than that of the ANL probe. Tests to determine the source of this
difference showed the presence of trace carbonaceous impurities in the
gas train of the carbon-detection system associated with the UNC probe.
[The carbon that diffuses through the iron membrane is converted first
to CO and then to CH_4, which is continuously monitored by a flame-
ionization detector (FID).] Revisions that have been made in the gas-
train piping of both probes now allow more accurate instrumental compen-
sation for trace carbonaceous impurities in the detection systems. This
compensation is particularly important at the low carbon fluxes being
monitored in the TEA.

After these changes were made, measurements taken over a one-
month period, during which time no significant change was made in the
carbon content of the sodium in the test apparatus, showed that both
meters gave carbon flux readings of 0.001 $\mu g/(cm^2)(min)$ with a standard
deviation of ±25%. This deviation is reasonable considering that it
includes not only instrumental variables but loop variables, both of
which must be held constant over long periods of time.

The effect of TEA operating variables on the response of the
meters was also investigated. In one experiment, the temperature in
the cold trap was increased from 225 to 278°C whereupon the carbon flux
(UNC probe) increased 30% in ∿1 hr, but returned to its original value
in ∿3 hr. In another experiment, the loop temperature was increased
from 325 to 425°C (cold trap temperature 225°C). The carbon fluxes
for both probes increased temporarily but returned to their normal
values in a few hours. In the above experiments, the response of the
ANL-modified probe was much smaller than that of the UNC probe.

After the loop temperature was increased, continued random increases
(one to three transients in a 24-hr period) in the carbon flux of the UNC
probe were observed. (The ANL-modified probe did not show this behavior.)
In a transient, the flux was 1 1/2 to 3 times the normal value, but
returned to normal within ∿15 min for a small increase to ∿2-3 hr for a
larger increase.

These observations suggest that carbon or carbon-containing
particulates are detached from the walls of the system by some distur-
bance and are released into the sodium and carried past the carbon
meters. To test this hypothesis, the system was disturbed on several
occasions by rapping the piping. This usually caused a large increase
in the carbon flux after ∿5 min, which corresponds to the time required
for diffusion of carbon through the probe membrane. In another test,
the primary sodium flow rate was abruptly changed from 1 gpm (the normal
flow rate) to 3 gpm. The results, plotted in Fig. I-4, show that the
carbon flux increased rapidly ∿5 min after the increase in sodium flow
was made, reached a maximum of about 10 times the original carbon flux
in 20 min, and then slowly returned to its original reading. These
results support the hypothesis that carbon or carbon-containing particu-
lates are present in the loop. Disturbing the system by rapping the
piping or increasing the sodium flow may have caused these particulates
to be swept up from the piping walls, thereby increasing the carbon
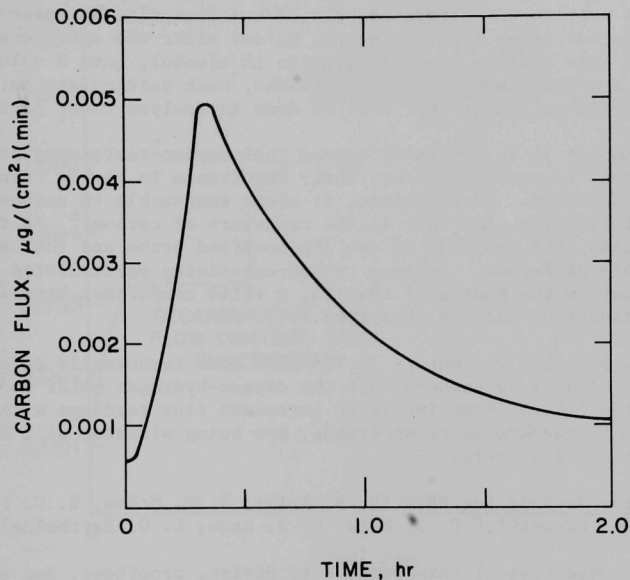
Fig. I-4. Response of UNC Carbon Meter to Increase
in Primary Sodium Flow in TEA

activity in the carbon meter.

An attempt was made to increase the carbon flux by introducing carbon into the loop; this was done by placing a number of pieces of Fe-5% C in the high-temperature test section of TEA. The temperature in the test section was then increased to 630°C (the loop was at 425°C), whereupon the carbon flux increased. Figure I-5 shows the carbon flux output from the UNC probe after the test section reached 630°C. After about 2 days, a constant flux was obtained. When the temperature of the test section was decreased, the carbon flux also decreased. A sample of sodium was taken from the sample holder after the specimens were removed; this sodium, upon dissolution in alcohol, gave a solution containing a large amount of finely divided, dark particulate matter, possibly carbon; an attempt will be made to analyze these particulates.

Although it is generally agreed that carbon-containing particulates are present in sodium systems, their importance in carbon transfer is not fully understood. Nevertheless, it seems reasonable to assume that these particulates play some role in the transport of carbon.[6] In the above experiments, the response of the ANL-modified probe and that of the UNC probe were different. Because carbon-containing particulates appear to be present in the sodium of the TEA, a valid comparison between the two probes cannot be made at this time.[7]

Tests of the two meters on TEA have been temporarily deferred because TEA will be used to test the oxygen-hydrogen meter module (described in Section I.D.). Experiments to correlate flux readings with the carbon content of standard metal specimens, now being planned, will be conducted in stirred sodium pots.

D. Meter Modules for FFTF (V. M. Kolba, J. M. McKee, E. C. Filewicz,[8] M. A. Slawecki,[8] P. J. Mack, D. J. Raue, L. G. Bartholme)

The objective of this work is to design, prooftest, and establish commercial availability for on-line meter modules to be installed at FFTF. These modules include flow and temperature controls as well as the meters for monitoring impurities. The prooftesting will be carried out on laboratory sodium systems and on the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II. Two types of modules are being designed and fabricated: (1) an oxygen-hydrogen meter module containing two oxygen meters (in case one

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[6] R. Roy and G. P. Wolzadlo, Nucl. Technol. 10, 307 (1971).

[7] Other reasons why a valid comparison of the two probes cannot be made are that (1) the flow characteristics of the two probes are not identical and (2) the temperature of the sodium drops about 15 to 30°C just before reaching the ANL probe (because of a pump in the system) and this may cause precipitation of carbon.

[8] E. C. Filewicz, EBR-II Project, is preparing the mechanical and structural designs and M. A. Slawecki, Chemical Engineering Division, is preparing the electrical designs for the oxygen-hydrogen meter modules, specimen equilibration-carbon meter modules, and the RSCL (Cell B and Cell C) installations.
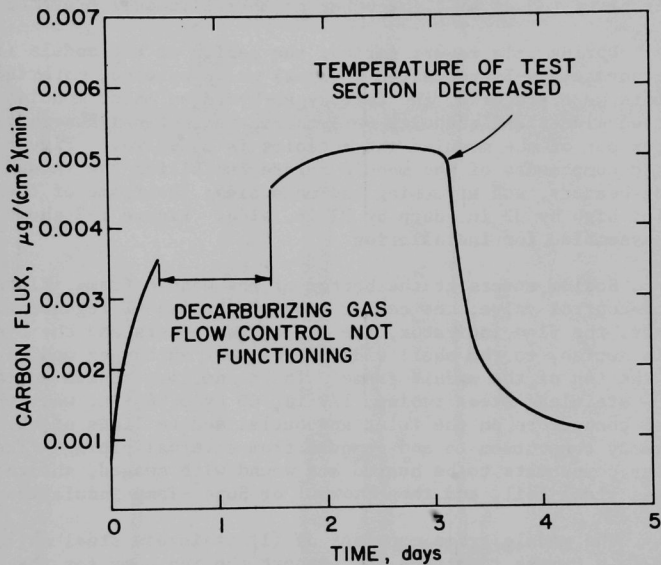
Fig. I-5.   Response of UNC Carbon Meter to Intro-
            duction of Fe-5% C into Sodium (tem-
            perature of test section, 630°C)

should fail) and a hydrogen meter and (2) a carbon-meter module, which, by substitution of a specimen holder for the carbon probe, will also serve as a module for equilibrating metal specimens.

1. Oxygen-Hydrogen Meter Module

The oxygen-hydrogen meter module contains two oxygen meters and one hydrogen meter in series with a regenerative heat exchanger, flow control valve, and flow indicator. Two of these modules are being built; one will be tested at ANL, the other at EBR-II in Cell B of the RSCL.

During this report period, the design of the module (revised to incorporate EBR-II requested changes) was completed, materials and components were procured, and two oxygen-hydrogen meter modules and associated electrical consoles were fabricated. Final assembly and check-out of the modules and consoles is under way. Figure I-6 shows the basic components of the module before installing the vacuum system, wrapping heaters, and attaching thermocouples; the frame of the module is 30 in. high by 32 in. deep by 22 in. wide. Figure I-7 shows the module assembled for installation.

Sodium enters at the bottom of the module frame, flows through the flow-control valve, the center tube of the 4.5-kW regenerative heat exchanger, the flow indicator, the two oxygen meters and the hydrogen meter in series, to the shell side of the heat exchanger and finally out at the top of the module frame. The connecting sodium ducts are Type 304 stainless steel tubing, 1/2-in. OD by 0.065-in. wall thickness. Conoseal connectors on the inlet and outlet sodium lines of the module allow ready connection to and removal from external piping. The piping and other components to be heated are wound with swaged, sheathed heaters, stainless steel foil, and then Kaowool or Super-Temp insulation.

The module frame consists of (1) stainless steel angles with intermediate braces to attach and support the ion pump for the hydrogen meter, and (2) various hangers and support brackets. Electrical connectors and gas lines pass through either the top of the module near the front, or the face of the module. A leak-tight pan comprises the bottom of the frame.

Two major components make up the oxygen meter (see Section A, above): a housing, which is installed in the piping of the module, and a removable electrolyte assembly. Sodium enters near the bottom of the housing and flows past the probe and out of the housing opposite the probe. A freeze seal is maintained between the electrolyte tube and the housing by air cooling the finned region. The oxygen meters have air reference electrodes, with gas valves on the inlet and outlet lines. The voltages from the two cells are selectively displayed on differential voltmeters or recorded by a 2-pen Honeywell recorder.

The hydrogen-activity meter can be operated in two modes (see Section B, above). The first is an equilibrium mode, in which the equilibrium hydrogen pressure above the sodium will be measured; the second is a dynamic mode, in which the hydrogen flux through the membrane will be monitored by the current from an ion pump. The data obtained
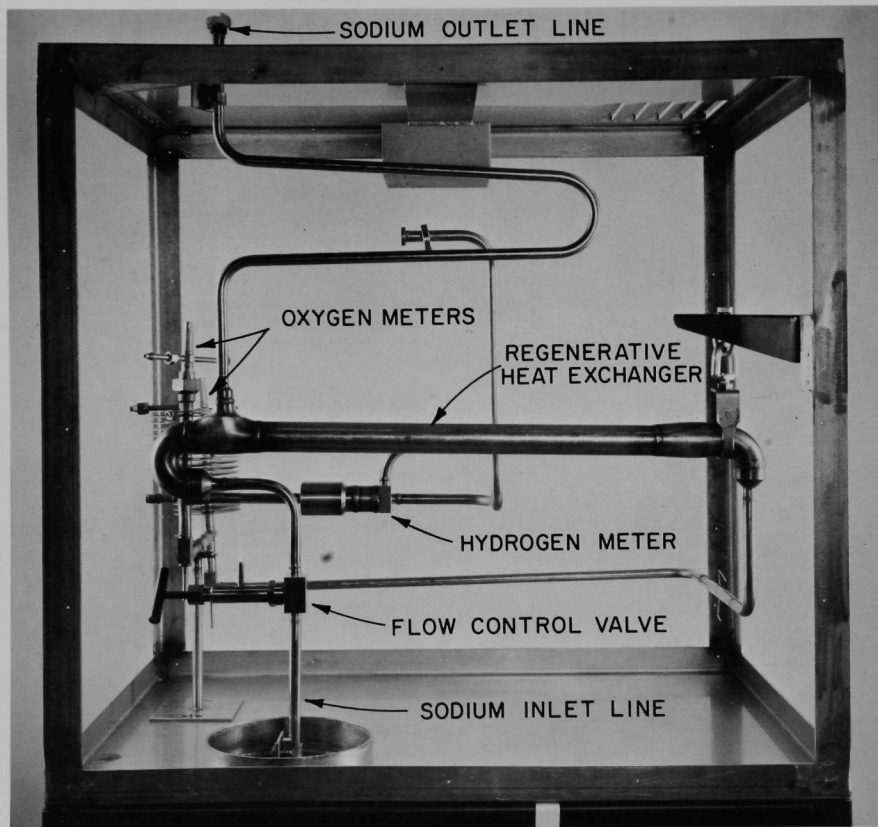
Fig. I-6. Oxygen-Hydrogen Meter Module--Side View
(30 in. high, 32 in. deep, 22 in. wide).
ANL Neg. No. 308-2458A.
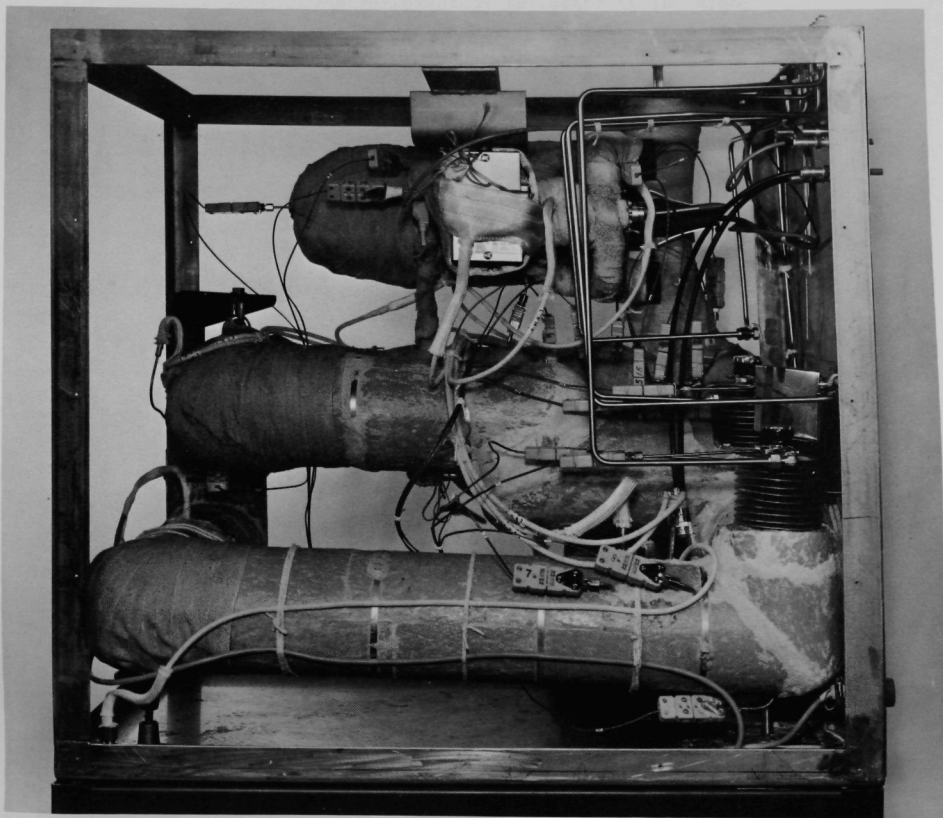
Fig. I-7. Oxygen-Hydrogen Meter Module Assembled for Installation—Side View. ANL Neg. No. 308-2477.

during operation in the equilibrium mode will be used to calibrate the meter for use in the dynamic mode. The membrane through which the hydrogen diffuses consists of reinforced nickel tubes welded in a stainless steel housing. Sodium flows across the outside of the membrane and a vacuum is maintained on the inside. Two manually operated vacuum valves, normally open when in the dynamic mode, serve to isolate the membrane from the ion pump during operation in the equilibrium mode.

The heat exchanger is a counter-flow, single tube-in-shell exchanger designed to maintain the outlet sodium temperature within ±50°F of the inlet sodium temperature. The flow-control valve is a manually operated Nupro Series U, bellows-type valve. The magnetic flow indicator, which was developed by the EBR-II Project, is a high-sensitivity indicator and has a response of ∿4.7 mV/gpm at 700°F.

Sodium line heaters are swaged coaxial or biaxial stainless steel-sheathed heaters. Thermocouples are swaged, stainless steel-sheathed, chromel-alumel. All leak detector probes in the module are sheathed, coaxial probes.

Silicon control rectifiers are used for temperature control (0-1000°F); these are provided with stepless proprotioning and reset control and with an adjustable voltage limiter for manual voltage limiting, if this is necessary. Heaters on piping outside the module, on the exit line from the regenerative heat exchanger, and on the vacuum manifold are controlled by 0-1000°F on-off controllers. Connectors are provided on the module for all instrumentation, control, and power cables from the consoles.

Safety alarms and system shutdown are provided for the following conditions: (1) high temperature of the sodium, (2) low temperature of the sodium, (3) high temperature in the oxygen-meter freeze seal, (4) low sodium flow, and (5) sodium leaks. Alarms are provided to indicate (1) high oxygen level, (2) high and low hydrogen level, and (3) high pressure in the ion pump of the hydrogen meter. Low-temperature interlocks are used for sequence heating and for proper automatic operation of the valves of the sodium supply system.

Module for EBR-II (RSCL, Cell B). As stated previously, the oxygen-hydrogen meter to be installed at EBR-II has been fabricated and is being tested prior to shipment.

The parameters applicable to the operation of the oxygen-hydrogen meter module in the RSCL are given in Table I-4. Initially only one module will be installed in the RSCL, Cell B; a second module will be added when the module becomes commercially available. However, piping, gaslines, electrical leads, etc. will be installed for both modules. A schematic diagram of the two modules and associated piping is shown in Fig. I-8.

The data package for module installation has been approved by EBR-II. Most components for the Cell B subsystems have been sent to EBR-II, and installation of the piping is under way.
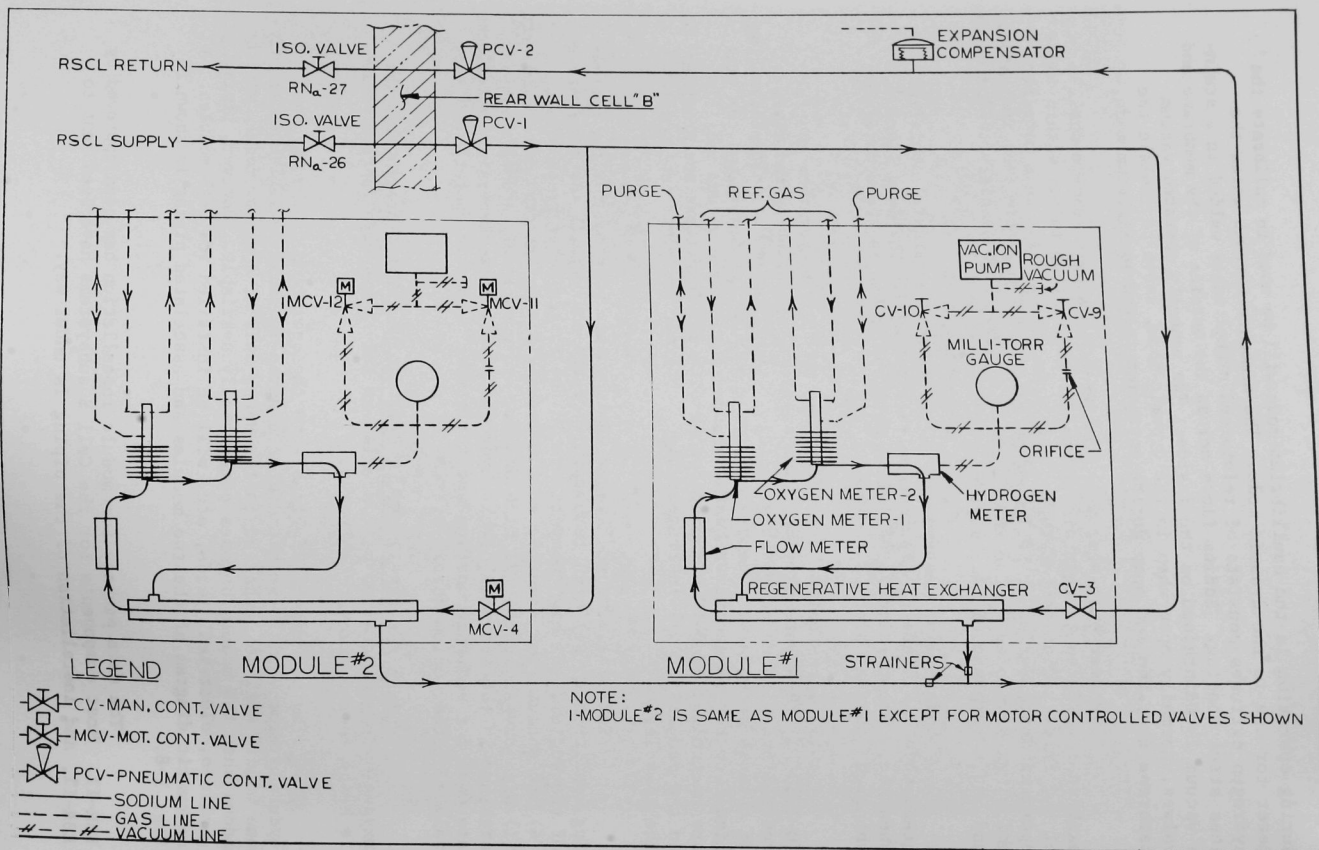
Fig. I-8. Schematic Diagram of Oxygen-Hydrogen Meter Modules for EBR-II (RSCL, Cell B)

TABLE I-4. Operational Parameters for Oxygen-Hydrogen
Meter Module in RSCL, EBR-II

Sodium inlet temp, °F	400-900
Sodium outlet temp, °F	Within 50°F of inlet
Design pressure, psig	50
Sodium flow rate, nominal, gpm	0.25
Oxygen sensor temp, °F	700-900
Hydrogen sensor temp, °F	700-900
Insulation surface temp, °F	∿140
Oxygen-meter electrolyte tube (thoria-7.5 wt % yttria)	
OD, in.	∿0.250
Wall thickness, in.	∿0.062
Hydrogen-meter nickel membrane	
Thickness, in.	0.010

2. Specimen Equilibration–Carbon Meter Module

The design of the specimen equilibration–carbon meter module has been completed, materials and components have been ordered, and fabrication of most items for two modules has been started. One of the modules will be tested at ANL; the other will be installed in Cell C, RSCL at EBR-II.

One of the problems that had to be considered in designing the module was that gas bubbles may enter the module with the incoming sodium. Hang-up of these bubbles could cause difficulties, such as poor heat transfer and irregular flow; therefore, the sodium flow rate must be high enough to sweep entrained bubbles out of those sections where flow is downward. To determine the required flow rate as a function of flow area, tests were performed in glass tubes using air bubbles in water to simulate gas bubbles in sodium. The tubes were tilted 45 degress because the maximum flow rate is required at that angle. In the system tested, the required flow rate was found to be 0.08 gpm for the 0.37-in.-ID tubing typically used for module piping. It is expected that gas bubbles will rise more slowly in sodium because it is slightly less dense and more viscous than water; hence this value provides a small factor of safety.

The heat exchanger in the specimen equilibration–carbon meter module is tilted 40 degrees from horizontal, and sodium flows downward through the annulus. Water tests with a mockup of this annulus indicated that the flow rate should exceed 0.9 gpm to prevent gas entrapment. Since the actual sodium flow rate will typically be 0.1 gpm, the annulus was modified to include a spiral baffle that reduced the effective flow area from 0.42 to 0.1 in.^{2}. This modification eliminated gas entrapment.

Module for EBR-II (RSCL, Cell C). The final data package for installation of the specimen equilibration–carbon meter module at EBR-II has been completed and sent to EBR-II for review and approval.

3. Module Designs for FFTF

Revised requirements related to the physical layout and design of the on-line impurity monitoring modules for FFTF have recently been received from WADCO. These requirements necessitate a revision in the design of the modules as presently conceived. Redesign of both the oxygen-hydrogen meter and the specimen equilibration–carbon meter module has begun, with WADCO requirements being incorporated. Most of the drawings will have to be redone, as will the stress and flexibility analysis for the module piping.

E. Detection of Leaks in Steam Generators (C. C. McPheeters, D. R. Vissers)

1. LMEC Leak Detection System

Work continued on the fabrication of a steam generator leak detector for use on the Sodium Components Test Installation (SCTI) at the Liquid Metal Engineering Center (LMEC) during their tests of the AI-designed steam generator. The leak detector operation depends on diffusion

of hydrogen from sodium through a nickel membrane into a dynamic vacuum system. Changes in the hydrogen concentration in the sodium are detected by changes in current in the vacuum-system ion pump. A rapid increase in this current activates an alarm system.

The vacuum-system ion pump operates with a 5000-V input, and currents of 10 to 100 µA are normally drawn. The SCTI installation requires cable lengths of approximately 150 ft; therefore, the possibility that significant current leakage could occur over that length was tested. It was found that the current leakage directly attributable to the long cable length was insignificant; however, at ambient temperatures of 100 to 150°F, the leakage was approximately 0.7 µA, which is significant at low hydrogen levels. Ambient temperature changes are generally slow, however, and this current leakage should not cause inadvertent alarms or other serious problems.

The requirements of the nickel membrane to be used in the leak detector are (1) that it provide sufficient surface area and be thin enough to diffuse hydrogen at a rate that matches the pumping speed of the ion pump and (2) that it have sufficient strength to withstand the pressure of the sodium system. The membrane used in the leak detector for LMEC is a nickel tube 0.250-in. ID by 0.009-in. wall thickness by 2 in. long. Reinforcing rings are placed inside the tube at equal intervals along the length to prevent collapse at high pressure.[9] When this membrane configuration was hydrostatically tested, the tube collapsed in independent sections between the reinforcing rings at a different pressure for each section. The minimum collapse pressure was 650 psi at room temperature. This is equivalent to 250 psi at the operating temperature of 900°F; this pressure is well above the operating pressure (100 psi) of the SCTI.

During this reporting period, fabrication of the leak detector was completed, including machining, welding, inspection, and installation of heaters, thermocouples, wiring, and insulation. Figure I-9 shows the leak detector completed except for installation of the sheet metal cover. The unit was shipped to LMEC on March 30, 1971. The document submittal requirements of LMEC were satisfied and an operating manual was written for the personnel of LMEC to use in installation and operation of the unit. Completion of the instrument package for the leak detector awaits the shipment of some of the alarm-system components from the manufacturer.

2. LMFBR Steam-Generator Leak Detector

A greatly simplified steam-generator leak detector is being designed for installation on EBR-II and as a prototype for future LMFBRs.

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[9] The magnetically formed nickel membrane discussed earlier (ANL/ST-8, p. 24) was found to be unsuitable because of fabrication difficulties. The present configuration is relatively simple to fabricate and the reinforcing rings provide sufficient strength to resist collapse at the operating temperature and pressure of the SCTI.

MEMBRANE HOUSING LOCATION

ELECTRICAL CONNECTIONS

ION PUMP

THERMOCOUPLES

SODIUM INLET

SODIUM OUTLET

PIPE PLUGS

ANGLE IRON FRAME
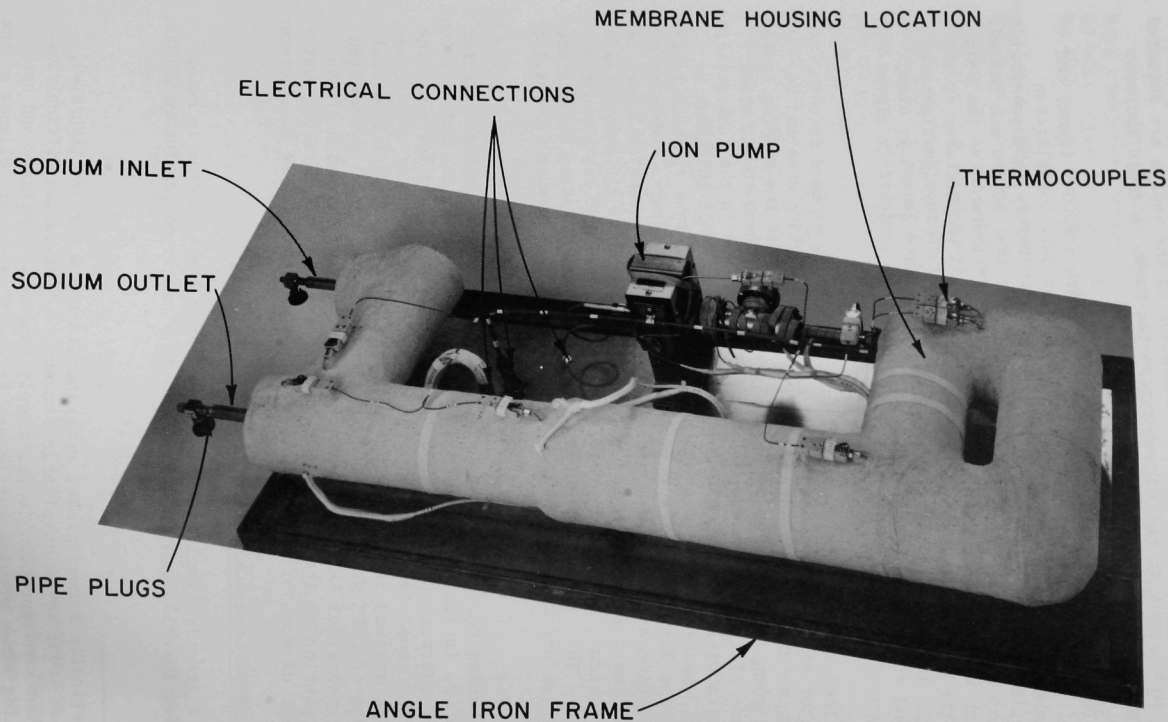
Fig. I-9.   ANL Steam-Generator Leak Detector to be Installed at LMEC.
ANL Neg. No. 308-2469A.

The design objectives for this leak detector are minimum time for sodium transfer through the detector piping to the nickel membrane, high reliability, and simplicity of design (low cost).

Design of a preliminary model has been completed and fabrication has been started. This model will be tested on an available sodium loop. The model consists of a regenerative heat exchanger, a sodium pump, a nickel membrane, a vacuum system, and associated heaters and instrumentation. One end of the heat exchanger is attached directly to the main sodium pipe. Sodium enters the annulus of the heat exchanger at this point and flows to a flow-dividing tee, where it is diverted to a side leg in which the sodium pump is located. Flow continues from the pump, back to the flow-dividing tee, and along the annulus to the high-temperature end of the heat exchanger where the membrane is located. The sodium then flows past the membrane and returns to the main stream through the center tube of the heat exchanger.

Fabrication costs, in the ANL shops, of leak detectors suitable for installation on EBR-II, have been estimated at about $9000 per unit for 10 units. This cost includes all hardware items as well as all instrumentation and alarm systems.

An important component in this design is the sodium pump. Current plans are to use an annular linear induction pump consisting of a linear motor with high-temperature (250°C) coils and an iron center tube which serves as a magnetic flux return. Sodium is pumped along the annulus between the coils and the iron tube. Motors with these high-temperature coils have been ordered for testing on a sodium system, and inquiries are being made about higher temperature (>250°C) coils.

F. Characterization of Impurity Meters and Meter Response to Impurity Species (C. C. McPheeters)

The primary goal of this work is the determination and interpretation of nonmetallic impurity levels in cold-trapped sodium as a function of cold-trap operating parameters and procedures. The methods for determining the impurities (O, C, H, and N) in the sodium will be on-line impurity monitoring, and sampling and analysis. Experimental work will be performed in a pumped-sodium apparatus (Apparatus for Monitoring and Purifying Sodium, AMPS) that will provide stable but adjustable impurity levels in the sodium fed to the test cold trap.

AMPS will be equipped with on-line instrumentation including an oxygen-hydrogen meter module and a sampling module on both the inlet and outlet of the experimental cold trap. Additional instrumentation will include a specimen-equilibration module and a sodium distillation sampler. A cold trap and hydrogen trap (titanium or zirconium) will be used to control the oxygen and hydrogen concentrations, respectively. Changes in oxygen and hydrogen concentrations across the experimental cold trap will be measured. The effect of the presence of hydrogen at various concentrations on the activity of oxygen as measured by the oxygen meters, and the effect of oxygen on the hydrogen activity will be studied. The interaction

of these two species and their combined effect on the on-line meter operation will be determined.

The piping and equipment layout for AMPS has been completed and stress analysis calculations for the piping have been performed on the entire system. Detail design of the system is in progress. Work has been started on the electrical system design, and work is in progress on the component-fabrication packages. Construction of the sodium system is scheduled to start in July 1971.

II. ANALYTICAL STANDARDS PROGRAM
(R. J. Meyer)

A. <u>Administrative Activities</u> (F. A. Cafasso, R. J. Meyer, M. H. Barsky, M. F. Roche)

    1. <u>Purity Specifications for Sodium and Cover Gas</u>

        Argonne National Laboratory has been given the responsibility for generating all RDT standards related to purity specifications for sodium and gases used in reactors or other sodium systems. These documents will specify the impurity levels that are acceptable for the purchase of sodium and cover gas and for the operation of sodium and cover-gas systems. They will also specify the sampling and analytical methods to be used to monitor all impurities and to demonstrate that certain impurities (for which methods of control exist) are at or below the acceptable levels.

        Preliminary specifications have now been generated and published in an informal document (ANL/ST-5) entitled "Interim Purity Specifications for Large Operating Sodium Systems." This document contains specifications for (a) purity of purchased sodium, (b) measurement and control of the level of selected impurities in sodium, (c) measurement of the level of other impurities in sodium, (d) measurement of the levels of impurities in cover gas, and (e) frequency of analysis of sodium and cover gas. The document also describes the criteria and the rationale that were used to arrive at these specifications. These preliminary specifications will be used as a basis for generating and/or revising the appropriate RDT standards.

        <u>Sodium Purchase Specifications</u>. A draft of RDT-M13-1 Revision 1, "Reactor Grade Sodium--Purchase Specifications," is nearing completion. The contents of this standard have been discussed with and are acceptable to all three potential suppliers[1] of reactor grade sodium. One potential user, namely, FFTF, has expressed concern that the preliminary specification for uranium (1 ppm) is high enough to cause difficulties in detecting and locating the fuel-element failures. Accordingly, ANL is reviewing this specification. As a part of this review, sodium samples from several sources are being analyzed to establish the uranium content that is currently achievable by the suppliers. If these data show that a lowering of the uranium-impurity specification is warranted, a change will be made. Upon completion of these analyses, a revised draft of this standard will be distributed to the users of reactor-grade sodium for review and comment. Distribution of this draft is scheduled for April 1971.

        <u>Cover-Gas Specifications</u>. Revision of the current version of RDT-M14-1 "Sodium Cover Gas" has begun. It is expected that a revised draft of this standard will be distributed to the users for review and comment in July 1971.

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[1] E. I. duPont deNemours & Co., U.S.I. Chemicals, and Ethyl Corp.

<u>Purity Specifications for Operating Sodium Systems</u>. The remaining sections of the document ANL/ST-5 will be incorporated into a new RDT standard titled "Purity Specifications for Large Operating Sodium Systems." In conformance with the established procedure, ANL has submitted a proposal to the RDT Standards Office of the Liquid Metal Engineering Center (LMEC) describing the scope of and the need for the new operating standard and requesting assignment of a number.

2. Interim Methods Manual

The report, "Interim Methods for the Analysis of Sodium and Cover Gas," has been revised, and publication of the report as ANL/ST-6 is scheduled for April 1971.

3. Use of Tetraboron Carbide (B_4C) Control Rods in FFTF

At the request of the Coolant Chemistry Branch of RDT, an examination has been made of the analytical and chemical problems associated with the use of B_4C in FFTF. Current plans at FFTF call for neutron control by means of B_4C. Individual B_4C pins will be clad with stainless steel and assembled into control, shim, and safety rods. Typically, each rod will contain 10 kg of B_4C (1.5 kg ^{10}B).

The following problem areas were considered: stability of B_4C in sodium and in a fast flux, interaction of stainless steel with B_4C, analytical methods for the detection of leaks in control rods, tritium production, and gas blanketing. The conclusions, based on available information and on our own calculations, were as follows:

(1) Evidence indicates[2] that unirradiated B_4C is stable toward static sodium at 500°C for 200 hr. Its stability toward sodium after irradiation in a fast flux has not yet been firmly established, but preliminary findings on irradiations of B_4C, now in progress at WADCO,[2] give no indication that B_4C is rendered less stable to sodium by fast flux irradiation.

(2) Tests[3] conducted in the absence of sodium at temperatures as high as 800°C for 5000 hr revealed that Types 304 and 316 stainless steels do not interact with B_4C. However, in the presence of sodium and under similar conditions, an intermetallic layer was found to form on the surface of several steels. (Typically, the thickness of the reaction zone was 10 μm in tests conducted at 600°C for 2000 hr.) The formation

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[2] R. E. Dahl, WADCO, private communication.

[3] V. P. Smirnov et al, <u>The Interaction of Boron and Carbide with Austenitic Chromonickel Steel in a Medium of Sodium</u>, AEC-tr-7183 (February 1971).

of this layer did not appreciably affect the mechanical properties of
the steels; only a small loss in ductility was observed. Moreover, the
interaction of B_4C with steels in the presence of sodium was significantly
reduced by a protective chromium coating.

(3) The method currently used for the analysis of boron in sodium
has a detection limit of 0.2 ppm.[4] To raise the boron content of FFTF
sodium to 0.2 ppm would require dissolution or "washout" of an entire
control pin. Hence, chemical analyses for boron in sodium will be of
little value in either the detection or location of control-rod failures.
ANL has recommended a method that utilizes radium (radon) and xenon tags
simultaneously. The radium (radon) tags will be used to detect failures
in B_4C pins, and the xenon tags to locate them.

(4) Tritium will be produced in the B_4C rods via the $^{10}B(n,2\alpha)T$
reaction. We have estimated that in a fission flux of $10^{15} n/(cm^2)(sec)$,
approximately 2000 Ci of tritium will be produced in a six-month period
in B_4C rods containing $\sim$1.5 kg of ^{10}B. These estimates, based on current
core design, indicate that B_4C will be a major source of tritium in FFTF.

(5) Considerable quantities of helium will be generated from
(n,α) reactions on B_4C. Our calculations indicate that, if the B_4C pins
are not vented, $\sim$800 ml (STP) of helium will be contained in a single
B_4C pin at 1.5% burnout. The cladding of the control pins is designed to
withstand the pressure from this quantity of helium at the reactor tempera-
ture, but, should a defect develop, this quantity of helium might be re-
leased suddenly, causing gas blanketing problems similar to those that
can occur with driver fuel.

B.   Laboratory Activities

    1.   Interim Methods for Nonmetallic Impurities (M. H. Barsky, M. D.
          Adams, H. S. Edwards, R. C. Haglund)

    Efforts have continued on establishing capabilities for deter-
mining oxygen, hydrogen, and carbon by the interim methods. Inert-
atmosphere gloveboxes have been installed and are operational. All equip-
ment necessary for performing these analyses has been installed and checked
out. Shakedown tests of the methods are in progress.

    2.   Effects of Line Length on Sample Validity (S. B. Skladzien,
          W. E. Ruther[5])

    One of the ANL lead assignments related to FFTF needs is the
determination of the effects of sampling-line length on sample validity.
Of principal interest is the effect on the determination of (1) nonmetallic

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[4]Interim Methods for the Analysis of Sodium and Cover Gas, ANL/ST-6, p. 51,
Argonne National Laboratory (in press).

[5]EBR-II Project.

impurities, mainly oxygen, hydrogen, and carbon, (2) metals and halides, and (3) radioactive species.

In the first set of experiments, the effect of line length on the oxygen content of sodium was investigated in a flowing sodium system at 350°C (662°F). The equipment consisted of a main loop of ∿15-gal capacity and a smaller bypass loop of ∿1-gal capacity. The two loops were interconnected so that they could be operated independently or in series. The smaller loop consisted of 100 ft of 5/8-in. OD (9/16-in. ID) Type 304 stainless steel tubing with a UNC electrochemical oxygen meter located at each end of the 100-ft section. The experiments were performed by operating the two systems independently at different oxygen levels (see ANL/ST-8, p. 28) and then quickly (in ∿2 sec) interconnecting the systems in series by means of a valving sequence. The emf response of the oxygen meters was then recorded as a function of time.

Prior to the experiments, the oxygen meters were calibrated as a function of cold-trap temperature. For convenience, a recently published solubility curve[6] for sodium oxide was used to assign numerical values to the oxygen levels in sodium. This method of calibration was considered adequate because the relative performance of the meters, rather than the absolute measurement of oxygen levels, was the significant factor in these experiments.

The experiments were conducted at two different sodium flow rates and with the initial oxygen concentration in the main loop both higher and lower than in the bypass loop. In the first experiment, the sodium flow was 5 gpm, the bypass loop was initially at 7.5 ppm oxygen, and the main loop was maintained at 1.8 ppm oxygen. The second experiment was also conducted at a sodium flow of 5 gpm, but the bypass loop was initially at 0.4 ppm oxygen and the main loop was maintained at 2.1 ppm oxygen. Figure II-1 shows the recorder chart record for the second experiment. In the third experiment, the sodium flow rate was reduced to 2.5 gpm, and the initial oxygen levels were 9.7 and ∿1 ppm for the bypass and main loop, respectively. The results of the three experiments are given in Table II-1.

In each experiment, the inlet meter response was rapid and the response time of the outlet meter corresponded closely to the time calculated for the passage of sodium through the 100 ft of tubing at the known flow rate (see Table II-1). The changes in oxygen level were the same for both cells, within experimental error. From these data, it is concluded that at these flow rates and oxygen levels no significant loss in accuracy is incurred by the use of a sample-line length of 100 ft and that the oxygen-meter response to a change in oxygen level is limited only by the time required for the sodium to move through the line.

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[6] D. L. Smith and T. F. Kassner, "Application of Thermodynamic and Kinetic Parameters of the V-O-Na System to the Sodium Corrosion of Vanadium Alloys," Corrosion by Liquid Metals, Plenum Press (1970).
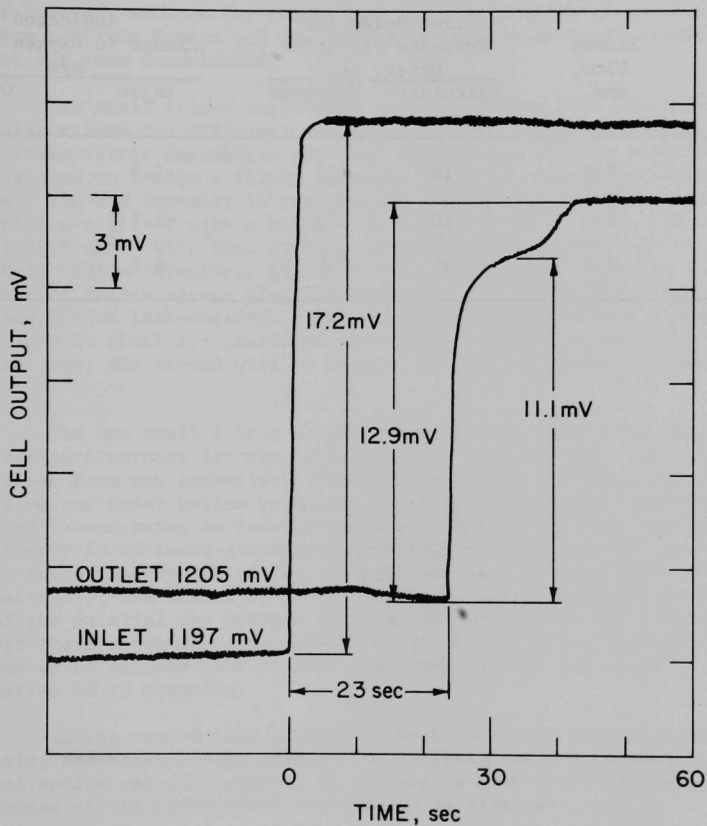
Fig. II-1. Responses of Electrochemical Oxygen Meters
to a Step Change in Oxygen Concentration
(Expt. 2)

TABLE II-1. Effect of Line Length on Responses of UNC Oxygen Meters (separated by 100 ft of tubing).

Expt. No.	Sodium Flow, gpm	Time Delay for Response of Outlet Meter, sec		Indicated Change in Oxygen Level, ppm	
		Calculated	Measured	Inlet	Outlet
1	5	18	25	−5.8	−5.7
2	5	18	23	+1.5	+1.5
3	2.5	36	39	−8.8	−9.0

3. <u>Particulate Analysis</u> (M. D. Adams)

As a part of the Analytical Standards Program, ANL will specify a method of particulate analysis for use in sodium technology programs. Most of the aspects of such a procedure have been reasonably well established; however, methods for recovering the particulates in an unchanged form from a filter device and for examining them in an inert atmosphere have not yet been established.

Two small filter assemblies were previously used to collect particulates from two different sodium loops (see ANL/ST-8, p. 30). The use of these filter assemblies provided information on flow restriction that was used to design a filter assembly for large operating sodium systems. The new assembly is constructed of Type 316 stainless steel and contains a filter with a nominal pore size of 10 μm and a surface area of 29.6 cm^2. With this design, filtration of 600 gal (∿1% of the EBR-II sodium inventory) should be possible in less than one day of operation unless severe plugging develops. Two assemblies have been built and helium leak-checked. One assembly was installed on a small sodium loop to check its characteristics with respect to flow rate and pressure drop; the second will be shipped to Idaho for installation on EBR-II.

The two small filter assemblies mentioned above were also used to investigate methods for the examination of particulates. The sodium was drained from one assembly by heating the filter cartridge and forcing the sodium out under helium pressure. Residual sodium was then distilled out under vacuum using an induction heater. The filter was removed from the assembly in an inert-atmosphere glovebox and examined with a microscope. Approximately 40% of the filter surface was covered with particulate material. The weight of particulates was estimated to be about 50 mg. Some of the material was scraped from the filter surface for identification. Although there appeared to be several kinds of particles, the major fraction was made up of agglomerates of very fine particles of one material. Further examination is in progress.

In the second test assembly, the bulk sodium was also removed by melting and pressurizing with helium to drain the molten sodium. The residual sodium was then removed by extraction with liquid ammonia. Examination of the particulate material is in progress.

4. <u>Determination of Low Levels of Carbon in Iron</u> (M. H. Barsky, A. F. Panek)

Iron is one of the metals under consideration for application in the equilibration method for the determination of carbon in sodium (see Section V.B.3, this report). One potential problem with its application, however, is that the expected carbon content (<10 μg) of the equilibrated iron wire may be at or below the sensitivity limit for carbon using commercially available equipment. This equipment (a Leco Carbon Analyzer) uses oxygen and a combustion accelerator to convert the carbon to carbon dioxide, which is measured with a thermal conductivity cell detector.

To increase the sensitivity of the instrument, the following modifications were made: The carbon dioxide was reduced to methane by addition of hydrogen and passage over a catalyst of nickel, chromium, and aluminum oxides heated to 350°C. The methane was measured by a flame-ionization detector, which increased the sensitivity for carbon measurement by one to two orders of magnitude. At this point, it became evident that the blank of the method, which is normally zeroed out electrically, was larger than the net signal expected from the sample. Hence, the increased sensitivity did not reduce the detection limit appreciably. Subsequent investigation indicated that the main contribution to the high blank was the carbon content of the tin and iron accelerators. Utilization of iron accelerator decarburized by reduction in a hydrogen atmosphere at 750°C and elimination of the tin accelerator reduced the blank by more than an order of magnitude.

These modifications will permit more precise measurements of the distribution coefficient of carbon between iron and sodium.

5. <u>Sampling and Analytical Procedure for Fission Products in Cover Gas</u> (M. H. Barsky, A. F. Panek)

High-temperature gas chromatography is being investigated as a means of separating fission-product gases and vapors from each other and from sodium vapor and aerosol.

The apparatus used for this investigation is all stainless steel and has been operated in the temperature range of 400 to 650°C. The carrier gas has been argon, and hydrogen and krypton have been used as representative permanent gases. A thermal conductivity detector has been used to sense the elution of permanent gases, and a flame has been used to sense the presence of sodium vapor.

Samples of permanent gases have been passed through 3-, 6-, 9-, and 12-in. chromatographic columns with no retardation observed.

III. FISSION PRODUCT AND COVER GAS TECHNOLOGY
(W. E. Miller)

One of the goals of this program is the development and testing of monitoring methods for characterizing fuel failures in LMFBR systems. The bases for development of these methods are (1) the determination of concentration levels of characteristic fission products released from a fuel failure and (2) the determination of rates of change in concentration levels of these fission products in reactor cover gas and sodium. This information is then related to the type of failure which produced the fission product release. The ultimate goal is to furnish a monitor that collects data as a fission product release is occurring and analyzes the data in terms of the characteristics of that particular failure. An additional goal of the program is the use of the detection and characterization monitors for failure location.

A. Failed Element Detection and Location (W. E. Miller)

1. Method for Locating Fuel Failures After Reactor Shutdown

One approach that might be taken for locating fuel failures in LMFBR systems, after reactor shutdown, involves intermittent restriction and release of sodium flow through selected fuel assemblies. In this concept, the sodium flow through each assembly is restricted, in turn, by a flow restriction device held in position by the fuel handling mechanism. (Complete flow stoppage is neither necessary nor desirable.) The resulting increase in pressure should force sodium into cladding defects. When the restriction is removed, a reduction in pressure occurs, and fission products should be released to the cover gas and/or the sodium coolant. Detection by a monitoring system during testing of a particular assembly thus provides the location of the failure.

The sodium pressures[1] outside a typical LMFBR fuel pin are shown in Fig. III-1 for the conditions of interest. The diagonal line on the figure gives the pressure profile along the fuel pin at full coolant flow. When sodium flow through a particular assembly is reduced to a lower level by a restriction at the top of the assembly, the pressure profile is that shown by the top curve on the figure. The driving force to push sodium into any defect along the pin is given by the difference of the two curves. For example, for defects at a bottom weld, core centerline, and a top weld, the driving forces are 11, 31, and 74 psi, respectively. When the flow restriction is removed, the pressure profile reverts to the diagonal curve and should result in a discharge of fission products from defective fuel pins.

This technique could give information on the type of failure as well as the location. For example, if the defect were in the top weld (gas leaker), the inflow of sodium would compress the gas in the plenum and only gas would be released when the stopper was removed from that assembly. If the defect were at the core centerline or bottom weld

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[1] Calculated from data in "1000 MWe LMFBR Follow-On Study, Task II," AI-AEC-12791, Vol. 1.

sodium containing fission products (nonvolatile as well as fission gases) would be also discharged when full flow was resumed. Note that the method discussed above would be applicable at any time after power shutdown: it could be applied at full or reduced flow conditions. One requirement is that a hydraulic balance exist at all cladding defects prior to the start of the search for leakers and that this balance be maintained (except for the assembly undergoing examination) throughout the search period.

2. Detection and Characterization of Fuel Failures

In the event of serious cladding failures, certain fission products, e.g., cesium, rubidium, iodine, and tellurium, should be easily leached from oxide fuel by sodium entering the fuel pin. Measurement of the concentrations and rates of change in concentration of certain isotopes of these fission products (and some of their daughters) in the coolant and in the cover gas is a potential means of characterizing failures. (The selection of isotopes for failure characterization was discussed in ANL/ST-2, pp. 3-1 to 3-7, and ANL/ST-3, pp. 3-2 to 3-5.) The development of a monitoring method that utilizes the determination of ^{135}I in the sodium coolant is reported in Section III.B, below. The discussion presented here is directed toward examining the different types of failures that can occur and the problems involved in characterizing them if cover-gas analysis is the only method available.

If a leak existed initially or developed early at the bottom weld, the gas in the plenum could be compressed to 0.4 of its original volume by the sodium pressure (95 psi) which exists at the defect at full sodium flow (see Fig. III-1). This would cause sodium to enter the fuel element and cover the fuel oxide. If one assumes a fission gas release of 50% from the oxide, a burnup of about 1% would be required to lower the sodium level to the top of the core oxide. During this irradiation period, the development of a sudden cladding failure (possibly as the result of swelling and stress buildup due to the formation of sodium-fuel oxide reaction product) below the sodium level would result in a burst discharge of sodium and gas. Fuel exposed in this manner could be vulnerable to washout since its structure would be altered. Although the sodium-fuel interaction product may form rather slowly, once the fuel oxide is exposed to high-velocity sodium, disintegration may be very rapid. A defective top weld could also lead to the ingress of sodium and subsequently to failure in the core region. However, in this case there would be no pressure force inside the fuel pin to pulse sodium or gas out through the new failure. This would be a case of exposed fuel with no initial burst release.

If cover-gas analysis is the only diagnostic tool available, the first type of failure (burst release) discussed above could easily be confused with a new cladding defect releasing only fission gas. The following example illustrates the problem. For the postulated failure, sodium containing some ^{135}I would be released, as well as fission gases containing its daughter ^{135m}Xe. The iodine release in the burst may be expressed as some fraction of the equilibrium amount that exists inside the cladding prior to failure. The xenon release may be expressed in the same fashion. The ratio of these two fractions, K, will determine
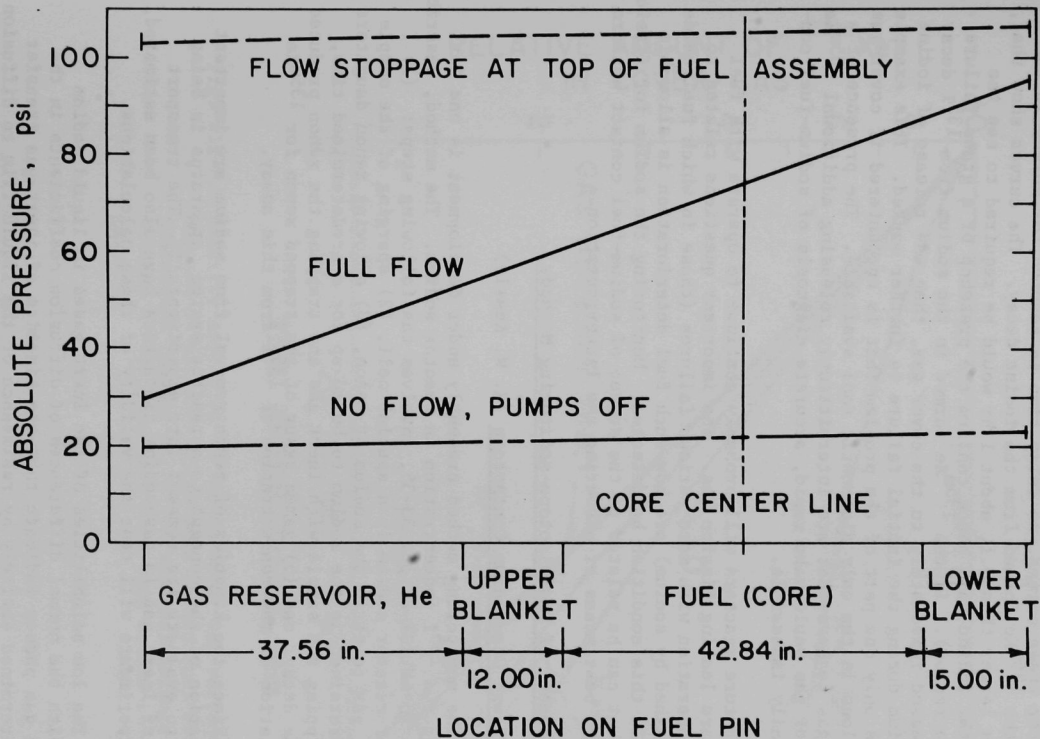
Fig. III-1. Pressures Outside Typical LMFBR Fuel Pins[1]

the amount of ^{135m}Xe that will appear in the cover gas (from the gas release and from the decay of ^{135}I in the sodium). Figure III-2 shows, for various values of K, the relative amounts of ^{135m}Xe in the cover gas, as a function of time, after the burst release.

For these curves, no delay time is assumed for holdup in the sodium of the ^{135m}Xe formed from the iodine decay. The curves show that, unless K is larger than 0.1, about 1 hr would be required to see the effect of the iodine (and hence confirm the presence of a gross failure in the core region). If the ^{135m}Xe formed in the sodium from ^{135}I decay is not released immediately to the cover gas, then the release of iodine to the sodium during the initial failure is further masked. This example illustrates only one part of the problem that is encountered if cover-gas analysis alone is the only diagnostic tool available. The presence of a number of gas leakers that are intermittently releasing additional ^{135m}Xe to the cover gas would make rapid, accurate diagnosis of sodium-fuel contact virtually impossible.

Future reactors will probably continue to operate with fuel pins that are leaking fission gas. The important questions related to continued operation with more serious failures (those in which fuel oxide is being washed by sodium) are how much fuel deterioration is allowable and how will this condition be detected. Monitoring the sodium for fission products that can be related to the degree of sodium-fuel contact appears to offer the best means of answering the latter question.

B. Development of Radioisotope-monitoring Methods

1. Inert Gas-Sodium Contactors (R. W. Kessie)

The monitoring method presently under development is one for determining the ^{135}I concentration in reactor sodium. The method, described previously in ANL/ST-8, pp. 33-35, involves the following steps: (1) sampling of reactor sodium in a special cell, (2) sparging of the sample with inert gas to strip the sodium of xenon, (3) allowing xenon daughters of iodine retained in the sodium to build up for a predetermined time, (4) restripping the sample with inert gas and trapping the xenon produced from iodine decay, and (5) gamma assay of the trapped xenon for ^{135m}Xe and calculation of the concentration of ^{135}I from this assay.

Since the kinetics of xenon removal from sodium are important for application of the concept to a reactor system, apparatus is being assembled to evaluate its removal rate experimentally. The transport kinetics of inert gas in gas-sodium contactors have also been estimated, and the experiments will test the validity of these calculations.

The low solubilities of the inert gases in liquid sodium combined with the normal differences of diffusion coefficients in the liquid and gas phases indicate that the kinetics of inert-gas transfer will be determined entirely by resistance of the liquid film to diffusion of gas.
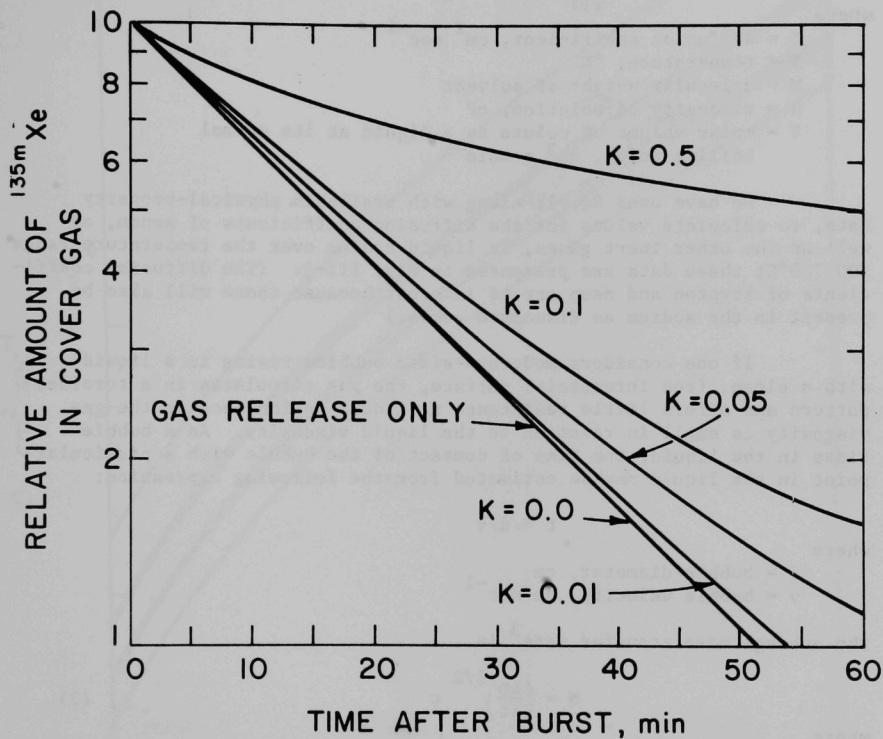
Fig. III-2. Relative Amount of ^{135m}Xe in Cover Gas Following Burst
Release of Gas and Sodium from Failed Fuel Pin (K =
fractional release of ^{135}I/fractional release of
^{135m}Xe; ^{135m}Xe transport time from sodium to cover
gas = 0)

The diffusion coefficients of solutes in dilute solution for unassociated liquids have been correlated,[2] with an average deviation of 12% between calculated and observed results, by the following equation:

$$D = 7.4 \times 10^{-8} \frac{TM^{1/2}}{\mu V^{0.6}} \tag{1}$$

where
 D = diffusion coefficient, $cm^2 \ sec^{-1}$
 T = temperature, $°K$
 M = molecular weight of solvent
 μ = viscosity of solution, cP
 V = molar volume of solute as a liquid at its normal boiling point, $cm^3 \ g\text{-mole}^{-1}$

We have used Eq. 1, along with available physical-property data, to calculate values for the diffusion coefficients of xenon, as well as the other inert gases, in liquid sodium over the temperature range 100-700°C; these data are presented in Fig. III-3. (The diffusion coefficients of krypton and neon are of interest because these will also be present in the sodium as dissolved gases.)

If one considers moderate-sized bubbles rising in a liquid with a clean, free interfacial surface, the gas circulates in a toroidal pattern and offers little resistance to liquid motion because the gas viscosity is small in relation to the liquid viscosity. As a bubble rises in the liquid, the time of contact of the bubble with a particular point in the liquid may be estimated from the following expression:

$$t = d/v$$

where
 d = bubble diameter, cm
 v = bubble velocity, $cm \ sec^{-1}$

The average mass transfer rate[3] is

$$N = \left(\frac{4D}{\pi t}\right)^{1/2} c \tag{2}$$

where
 N = flux, $g\text{-mole} \ cm^{-2} \ sec^{-1}$
 c = driving force of liquid film, $g\text{-mole} \ cm^{-3}$

or

$$N = \left(\frac{4Dv}{\pi d}\right)^{1/2} c \tag{3}$$

The time constant for removal of inert gas from the liquid phase is given by

[2] C. R. Wilke, P. Chang, *Correlation of Diffusion Coefficients in Dilute Solutions*, AIChE Journal 1, 264-270 (1955).

[3] R. Bird et al., *Transport Phenomena*, p. 541, John Wiley and Sons, Inc., New York (1963).
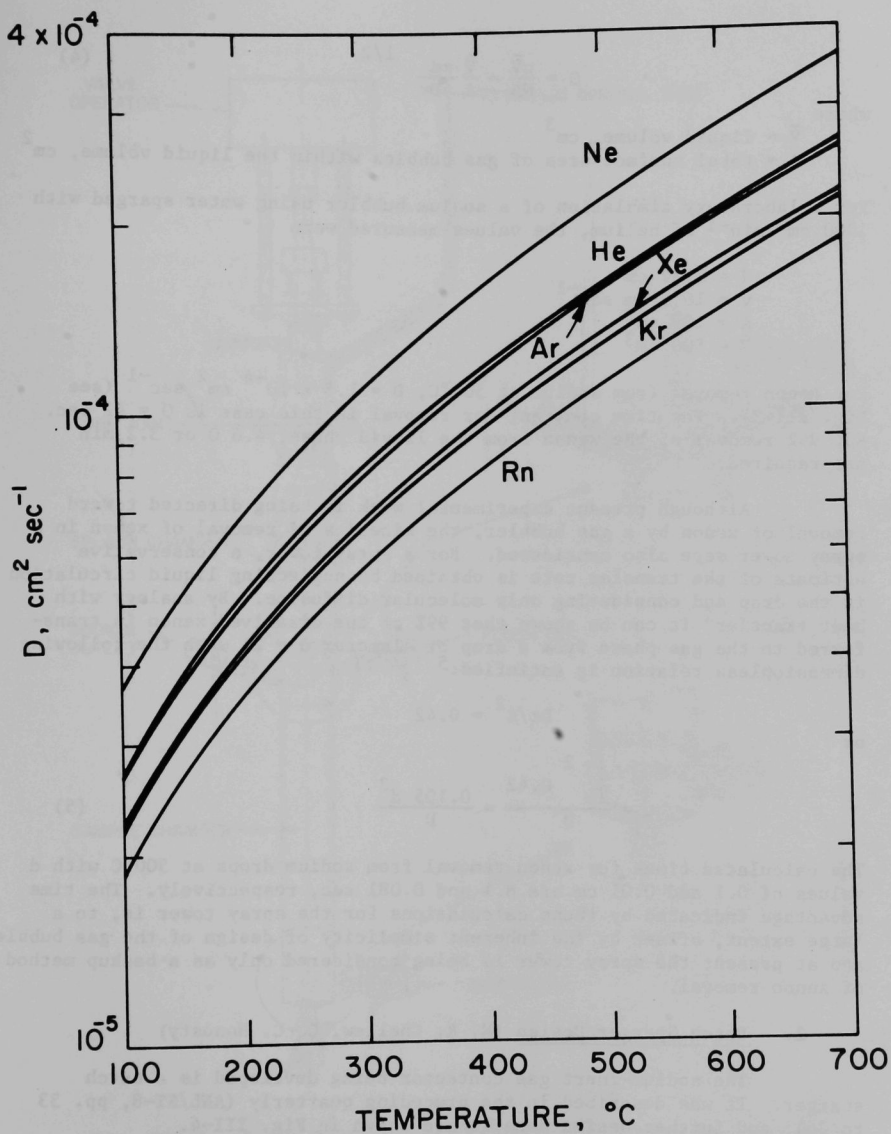
Fig. III-3. Estimated Diffusion Coefficients
for Inert Gases in Liquid Sodium

$$\Theta = \frac{c\bar{V}}{NA} = \frac{\bar{V}}{A} \frac{\pi d}{4Dv}^{1/2} \qquad (4)$$

where
$\bar{V}$ = liquid volume, cm^3
A = total surface area of gas bubbles within the liquid volume, cm^2

For a laboratory simulation of a sodium bubbler using water sparged with 1000 cm^3 min^{-1} of helium, the values measured were

d = 0.37 cm
v = 16.9 cm sec^{-1}
A = 138 cm^2
$\bar{V}$ = 500 cm^3

For xenon removal from sodium at 500°C, D = 1.3 x 10^{-4} cm^2 sec^{-1} (see Fig. III-3). The time constant for removal in this case is Θ = 42 sec. For 99% removal of the xenon from the liquid phase, 4.6 Θ or 3.2 min are required.

Although present experimental work is being directed toward removal of xenon by a gas bubbler, the kinetics of removal of xenon in a spray tower were also considered. For a spray tower, a conservative estimate of the transfer rate is obtained by neglecting liquid circulation in the drop and considering only molecular diffusion. By analogy with heat transfer[4] it can be shown that 99% of the dissolved xenon is transferred to the gas phase from a drop of diameter d = 2ℓ when the following dimensionless relation is satisfied:[5]

$$Dt/\ell^2 = 0.42$$

or

$$t = \frac{\left(\frac{d}{2}\right)^2 0.42}{D} = \frac{0.105 \, d^2}{D} \qquad (5)$$

The calculated times for xenon removal from sodium drops at 500°C with d values of 0.1 and 0.01 cm are 8.1 and 0.081 sec, respectively. The time advantage indicated by these calculations for the spray tower is, to a large extent, offset by the inherent simplicity of design of the gas bubbler, and at present the spray tower is being considered only as a backup method of xenon removal.

2. <u>Batch Sparger Design</u> (N. R. Chellew, C. C. Honesty)

The sodium-inert gas contactor being developed is a batch sparger. It was described in the preceding quarterly (ANL/ST-8, pp. 33 to 36), and further design details are shown in Fig. III-4.

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[4] H. S. Carslaw, J. C. Jaeger, <u>Conduction of Heat in Solids</u>, p. 234, Oxford University Press, London (1959).

[5] Ibid, p. 102.

VALVE
OPERATOR

→ TO SODIUM AEROSOL TRAP

SPARGE GAS
OUTLET VALVE

TUBE JOINT

SPLASH CHAMBER

SODIUM
OUTLET

FLUSH GAS

SAMPLE CHAMBER

SPARGE GAS
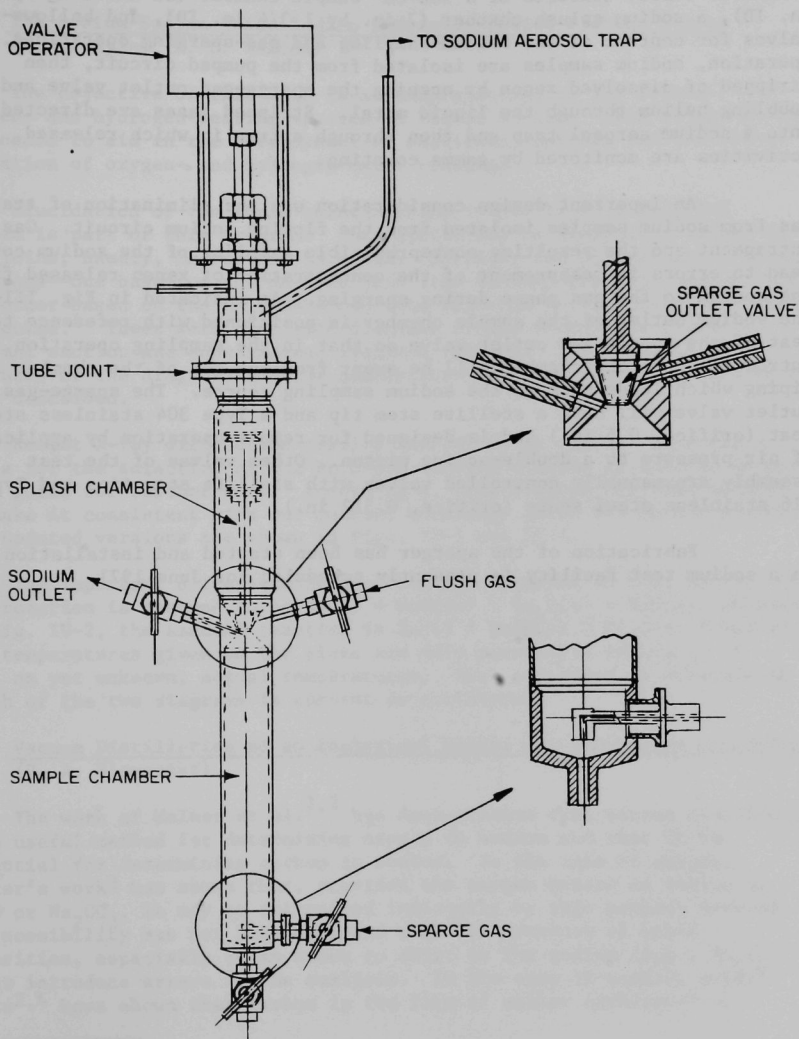
Fig. III-4. Batch Sparger for Stripping Xenon from Liquid Sodium

The prototype sparger, which is constructed of Types 304 and 316 stainless steel, consists of a 500-cm^3 sample chamber (11 in. long by 1 3/4 in. ID), a sodium splash chamber (7 in. by 1 3/4 in. ID), and bellows-sealed valves for control of the sodium-sampling and gas-sparging operations. In operation, sodium samples are isolated from the pumped circuit, then stripped of dissolved xenon by opening the sparge-gas outlet valve and bubbling helium through the liquid metal. Stripped gases are directed into a sodium aerosol trap and then through a trap in which released activities are monitored by gamma counting.

An important design consideration was the elimination of trapped gas from sodium samples isolated from the flowing sodium circuit. Gas entrapment and the resulting nonreproducible sampling of the sodium could lead to errors in measurement of the concentration of xenon released from the sodium to the gas phase during sparging. As indicated in Fig. III-4, the sodium outlet of the sample chamber is positioned with reference to the seat of the sparge-gas outlet valve so that in the sampling operation, gases introduced into the chamber will be swept from the top of the chamber into piping which leads back to the sodium sampling source. The sparge-gas outlet valve will have a stellite stem tip and a Type 304 stainless steel seat (orifice, 0.5 in.) and is designed for remote operation by application of air pressure to a double-acting piston. Other valves of the test assembly are manually controlled valves with stellite stem tips and Type 316 stainless steel seats (orifice, 0.312 in.).

Fabrication of the sparger has been started and installation in a sodium test facility is presently scheduled for June 1971.

IV. SODIUM CHEMISTRY
(F. A. Cafasso)

A. The Sodium-Sodium Oxide-Sodium Hydroxide-Sodium Hydride System
(K. M. Myles, R. D. Wolson)

The objective of this work is an understanding of the behavior of
oxygen- and hydrogen-bearing species in liquid sodium. This understanding
is needed to aid in the development of analytical methods and the inter-
pretation of oxygen- and hydrogen-meter readings.

Elucidation of the phase relationships in the $Na-Na_2O-NaOH-NaH$
system is part of this program. This system may be divided by either of
two joins, namely, Na-NaOH or Na_2O-NaH. Earlier, two preliminary working
diagrams--one based on the Na-NaOH join (the Na-NaOH working diagram) and
the other based on the Na_2O-NaH join (the Na_2O-NaH working diagram)--were
presented.[1] These were composite diagrams of the room-temperature iso-
thermal section and superimposed liquidus valleys. The essential
features of the diagrams and the assumptions made in generating them were
also described.

Recent X-ray diffraction results (ANL/ST-8, pp. 43-44) provided a
basis for the selection of the Na_2O-NaH working diagram as the one to use
as a guide for further work. Accordingly, this diagram has been updated
to make it consistent with our current knowledge about the Na-O-H system.
The updated versions are shown in Figs. IV-1 and IV-2.

The important difference between the two diagrams is that in Fig. IV-1
the reaction is assumed to be $Na(\ell) + NaOH(s) \rightleftarrows Na_2O(s) + NaH(s)$, whereas
in Fig. IV-2, the assumed reaction is $Na(\ell) + NaOH(\ell) \rightleftarrows Na_2O(s) + NaH(s)$.
The temperatures given on the plots are only reasonable estimates of
the, as yet unknown, actual temperatures. Work addressed to determining
which of the two diagrams is correct is continuing.

B. Vacuum Distillation as an Analytical Method for Impurities in Sodium
(R. A. Blomquist)

The work of Walker et al.[2,3] has demonstrated that vacuum distillation
is a useful method for determining oxygen in sodium and that it has
potential for determining carbon in sodium. In the case of oxygen,
Walker's work[2] has shown that, provided the oxygen exists in sodium as
Na_2O or Na_2CO_3, it may be determined indirectly by this method; however,
the possibility has not been explored that the presence of other
impurities, especially those known to exist in the sodium (e.g., Na_2C_2),
might introduce errors in the analysis. In the case of carbon, experi-
ments[2,4] have shown that carbon in the form of either carbonate[4] or

[1] ANL/ST-3, pp. 4-4 to 4-13; Figs. 4-2 and 4-5.

[2] J. J. Walker, E. D. France, and W. T. Edwards, Analyst 90, 727 (1965).

[3] J. J. Walker and E. D. France, Analyst 90, 228 (1965).

[4] V. M. Sinclair, J. L. Drummond, and A. W. Smith, TRG 1185(D) (1966).

Fig. IV-1. The Liquidus Valleys and Room-Temperature Isothermal
Section of the Na-Na$_2$O-NaOH-NaH System Based on the
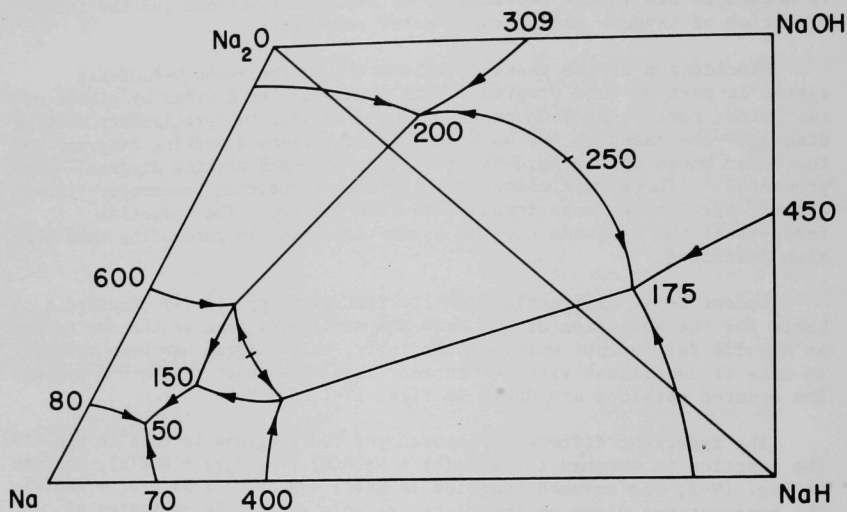Reaction Na(ℓ) + NaOH(s) $\rightleftharpoons$ Na$_2$O(s) + NaH(s)
(temperatures in °C)
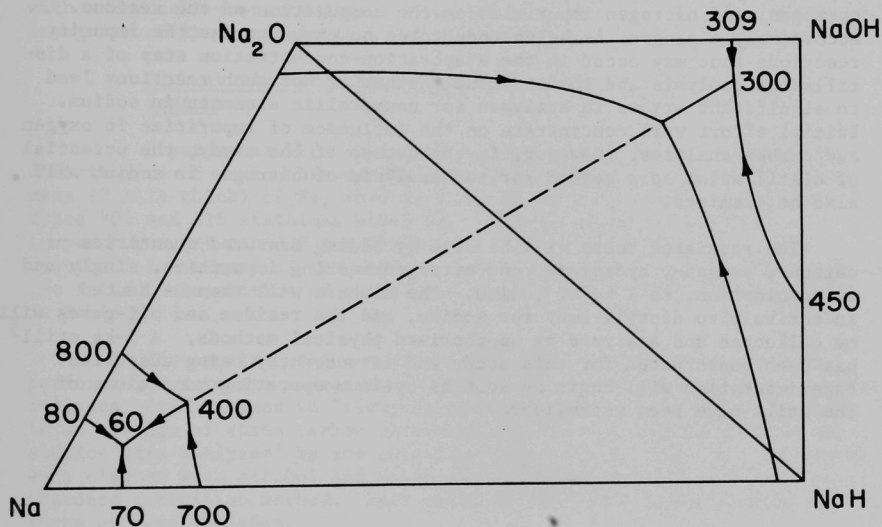
Fig. IV-2. The Liquidus Valleys and Room-Temperature Isothermal
Section of the Na-Na$_2$O-NaOH-NaH System Based on the
Reaction Na(ℓ) + NaOH(ℓ) $\leftrightarrows$ Na$_2$O(s) + NaH(s)
(temperatures in °C)

elemental carbon[2] is not lost (due to degradation of the carbonate or formation of carbon monoxide via the reaction of elemental carbon with sodium oxide) during distillation at 350°C. Tests to demonstrate that similar results are obtainable regardless of the form of the carbon or the type and concentration of other impurities in the sodium have not been done.

Clearly, to exploit the full potential of this method for oxygen and carbon analyses and to place the method on a firm and fully tested basis, experiments are needed that examine the effects of added carbon, oxygen, hydrogen, and nitrogen impurities on the composition of the residue. Accordingly a program is being undertaken to characterize the impurity reactions that may occur in the evaporation-concentration step of a distillation analysis and to determine whether or not such reactions lead to significant errors in analyses for nonmetallic elements in sodium. Initial effort will concentrate on the influence of impurities in oxygen and carbon analyses. However, in the course of the study, the potential of distillation as a method for the analysis of nitrogen in sodium will also be examined.

The requisite tests will be done by adding measured quantities of carbon-, oxygen-, hydrogen-, and nitrogen-bearing impurities, singly and in combination, to 1 kg of sodium. The mixture will then be heated inductively to distill away the sodium, and the residue and off-gases will be collected and analyzed by appropriate physical methods. A 1-kg still[5] has been constructed for this study and is currently being assembled. Experimentation will begin as soon as optimum operating conditions of the still have been established.

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[5]C. C. Miles of EBR-II, Idaho, provided the design of the still.

V. MATERIALS-COOLANT COMPATIBILITY
(T. F. Kassner)

A. Studies of Carbon Transport in Sodium-Steel Systems
(K. Natesan, T. F. Kassner, and C. A. Youngdahl)

The objectives of this work are an understanding of the mechanism and kinetics of carburization-decarburization processes involving austenitic and ferritic steels and the eventual correlation of results of these studies with mechanical-property data. Thus, predictions regarding the structural integrity of these steels in a reactor system will be made possible.

1. Distribution of Carbon Between Iron-Base Alloys and Liquid Sodium

Experiments were continued to obtain data on the equilibrium distribution of carbon between sodium and iron-base alloys. Foil specimens (2 mils thick) of Fe, Fe-8 wt % Ni, Fe-18 wt % Cr-8 wt % Ni, and Types 304 and 316 stainless steel were exposed to flowing sodium at temperatures between 600 and 750°C in a loop with a molybdenum test section. In several of the runs, a carbon source was present in the system. The initial composition of the alloys used in these experiments is given in Table V-1.

The experimental conditions and results for the experiments performed to date are summarized in Table V-2. Sodium samples for carbon analyses were obtained in "flow-through" samplers. Each value reported is an average of three carbon determinations on each sodium sample; the samples were analyzed[1] by the oxyacidic flux method. The foil specimens were cleaned with alcohol and water and then analyzed for carbon by a standard combustion method. Each value in the table is an average of three or more analyses.

The experiments show that in the absence of a carbon source in the system, the carbon concentration in the sodium is very low (≤ 1 ppm); however, carburization of Type 304 stainless steel occurred at temperatures between 600 and 750°C (runs 1 and 2). The presence of a carbon source increased the carbon activity in sodium, as evidenced by the increase in the carbon concentrations in the alloys and in sodium in runs 3, 4, and 6. In these latter runs the carbon concentration in the Fe-C alloy source decreased from an initial value of ~ 5 wt % to ~ 0.1 wt %; however, the material was still saturated at the conclusion of the runs. This indicates that the equilibrium between the carbon in sodium and the carbon in the saturated alloy was maintained during the entire run, since there is no kinetic limitation in transporting carbon from the source to the sodium in a loop of this size.

This method of adding carbon to the system can introduce some particulate graphite into the sodium as a result of graphitization of the heavily carburized source and the washing away of the surface particles by the flowing sodium. The carbon concentration in the sodium during the course of run 4 (carbon source present) showed a substantial decrease which may be attributed, in part, to the presence of graphite particles

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[1] Analyses performed by W. R. Sovereign, ANL-Idaho.

TABLE V-1. Composition of Iron and Iron-Base Alloys (concentrations are given in wt %; the remainder is iron)

Alloy	C	N	O	P	S	Cr	Ni	Mn	Mo	Si	Nb	Ti	Zr	V	Co	Cu
Fe	0.002	0.001	<0.005	<0.001	<0.005	<0.004	0.012	0.05	<0.002	<0.003	0.002	<0.001	<0.005	<0.001	0.001	0.00
Fe-8 wt % Ni	0.002	<0.001	0.016	<0.001	<0.005	<0.01	7.99	<0.01	<0.01	<0.01	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
Fe-8 wt % Ni -18 wt % Cr	0.0025	0.0019	0.008	<0.001	<0.005	17.74	7.92	<0.001	<0.01	<0.01	ND[a]	<0.01	<0.01	<0.01	<0.01	<0.01
Type 304 SS	0.047	0.045	--	<0.1	—	19.28	9.23	1.69	0.44	0.42	0.015	0.001	<0.001	0.2	0.05	0.2
Type 316 SS	0.074	0.033	—	<0.1	—	17.04	12.92	1.46	2.26	0.37	0.08	0.004	<0.001	0.1	0.05	0.2
Type 347 SS	0.064	0.049	--	--	--	19.21	11.09	0.94	0.09	0.62	0.68	0.015	0.12	0.2	0.05	0.1

[a]ND = not detected.

TABLE V-2. Experimental Conditions and Results of Carbon Distribution
Between Iron-Base Alloys and Sodium

Run No.	Run Time, hr	Temp., °C	Carbon Concentration in Exposed Foils					Carbon in Sodium, ppm	Cold-Trap Temp., °C	Remarks
			ppm in Fe	ppm in Fe-8 Ni	wt % in Fe-18 Cr-8 Ni	wt % in Type 304 SS	wt % in Type 316 SS			
1	750	700	--	--	--	0.090	--	0.70±0.39,	125	No carbon source.
		600	--	--	--	0.11	--	1.31±0.78		
2	3500	750	14	--	--	0.096	--	0.40±0.20	125	No carbon source.
		650	8	--	--	0.129	--	(at 800 hr), 0.70±0.20 (at 2000 hr)		
3	330	750	80	233	0.71	0.643	1.070	Sample not	125	Carburized Fe-8
		650	21	238	0.91	0.958	1.149	analyzed.		Ni source.
4	1000	750	89	97	0.96	0.897	0.940	25±1.0	125	Carburized Fe
		650	21	63	1.26	1.270	1.330	(at 300 hr), 1.8±0.4 (at 1000 hr)		source.
5	60	750	39	57	--	--	--	2.5±1.0	125	No carbon source.
		650	28	98	--	--	--	(at 58 hr)		
6	307	750	15	--	--	1.025	1.160	13.7±1.4	175	Carburized Fe
		650	12	--	--	1.193	1.279	(at 140 hr), 11.9±2.5 (at 300 hr)		source.

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that are eventually precipitated in the cold trap or other locations in the loop. The cold-trap temperature had a negligible effect on the final carbon concentrations in the steels exposed to sodium in these tests.

To achieve and control carbon levels in the sodium over a range that will result in carbon concentrations below 0.5 wt % in the stainless steels, a different method of adding carbon to the sodium has been devised. Thin-wall tubes of Armco iron were filled with graphite powder and welded closed. A number of these tubes were then inserted in a nickel vessel through which sodium will be flowed at temperatures between 450 and 600°C. On the basis of the equilibrium distribution of carbon between iron and sodium, it is expected that carbon concentrations in sodium in the range 0.3 to 7.0 ppm can be attained by this method. In addition to providing specific carbon levels by accurate control of the source temperature, the method will avoid introducing graphite particles into the loop sodium.

Further experiments to determine the equilibrium distribution of carbon between liquid sodium and the various steels will be conducted to obtain sufficient data for comparison with calculated carbon distribution curves.[2]

2. Measurements of Carbon Activities in Fe–Ni and Fe–Cr–Ni Alloys

Additional data to establish the activity of carbon in Types 304, 316, and 347 stainless steel as a function of the carbon concentration have been obtained at 600°C. The composition of the alloys and the details of the experiment were given in ANL/ST-8, pp. 47-50. The carbon concentrations in the three alloys, after an equilibration period of 2800 hr in Vycor capsules, are given in Table V-3. The range of carbon activities, as reflected by the carbon concentrations in the Fe-8 wt % Ni alloy in the three experiments, was not as large as was desired. Several additional runs at 600°C will be made at higher carbon levels to complete this work. Experiments to establish the carbon activities in the Fe-8 wt % Ni alloy as a function of carbon concentration and temperature (described in ANL/ST-4, pp. 52-55) are still in progress.

B. Determination of Nonmetallic Impurities in Sodium by the Equilibration Method (D. L. Smith)

The purpose of this work is to develop methods for accurately measuring the activities of nonmetallic elements, e.g., O, C, N, and H, in sodium at the low concentrations of interest for LMFBR application.

1. Development of the Vanadium–Wire Equilibration Method for Determining Oxygen Activity in Sodium

A procedure for determining the oxygen activity in liquid sodium by the vanadium-wire equilibration method has been reported.[3] The present effort in this area is directed toward (1) standardization and characterization of the method and (2) correlation of the results with oxygen meter measurements.

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[2] K. Natesan and T. F. Kassner, J. Nucl. Mater. _37_ (2), 223-235 (1970).

[3] D. L. Smith, Nucl. Technol. _11_ (1), 115-119 (1971).

**TABLE V-3. Carbon Analyses of Commercial Alloy Samples
Equilibrated at 600°C for 2800 hr**

Capsule No.	Carbon Concentration, ppm			
	Fe-8 wt % Ni	Type 304 SS	Type 316 SS	Type 347 SS
1	30.0	395	425	760
2	50.0	420	455	750
3	55.0	490	540	760

Standardization and Characterization. The vanadium-wire equili-
bration method[3] was developed from data for the distribution coefficients
of oxygen between sodium and vanadium at temperatures of 600, 650, 700,
and 750°C.[4] This method of analysis can be used at any temperature within
this range or 50°C on either side by interpolation or extrapolation of the
data. Equilibration of 0.25-mm-dia wire for 4 hr at 750°C is appropriate
for LMFBR applications, and these conditions have been recommended as a
standard to facilitate and improve comparison of interlaboratory analyses.
Additional distribution-coefficient measurements have been made under
these conditions to enhance the reliability of the values and to establish
the precision of the method. The results are given in Table V-4 and
plotted in Fig. V-1. The oxygen concentrations in the sodium were deter-
mined from solubility data[5] at the cold-trap temperature, which was care-
fully controlled in these experiments. The oxygen analyses of the vanadium
wires were obtained by an inert-gas fusion technique.[6] Analyses of wires
equilibrated simultaneously generally agreed within ±2%. Agreement of the
analyses was also good after the oxygen level was changed and then returned
to the previous level.

The oxygen concentrations in vanadium at 750°C reported previously[4]
were somewhat lower (for example, 10% at 1.0 wt % oxygen in vanadium)
than results obtained in the recent series of tests. This difference is
attributed primarily to difficulties in determining the oxygen concentration
in sodium at the lower levels, where vacuum distillation analyses were of
limited accuracy. A portion of the original data is now believed to have
been obtained under conditions in which the cold trap was slightly depleted
of oxygen; this resulted in values for the distribution coefficients that
were somewhat low. In addition, analytical problems[7] associated with the
gas-fusion apparatus occasionally resulted in low values for the oxygen
content of the vanadium wires. These analytical problems had the effect
of obscuring the slight depletion of oxygen in the cold trap and incom-
plete reequilibration of the loop after changing the temperature or oxygen
concentration. The small discrepancies in the distribution-coefficient
data have now been resolved, and the data presented in Table V-4 and Fig.
V-1 are considered to be more reliable than the previous values. These
data represent three series of tests which were conducted by cycling the
oxygen level in sodium several times from lower to higher values to con-
firm the reliability of the results. Control samples indicated that no
problems were encountered in the gas-fusion analyses of these vanadium
wires.

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[4] D. L. Smith, Met. Trans. 2 (2), 579-583 (1971).

[5] D. L. Smith, T. F. Kassner, Corrosion by Liquid Metals, J. E. Draley,
J. R. Weeks, eds., pp. 137-149, Plenum Press (1970).

[6] B. D. Holt, H. T. Goodspeed, Anal. Chem. 35, 1510-1513 (1963).

[7] Occasional losses of carbon monoxide in the gas-fusion apparatus being
used were due to (1) gettering by freshly deposited films of metals
having high vapor pressures (e.g., Al, Mg, Be) from previous analyses in
the same reaction chamber or (2) a contaminated chamber resulting from
excessive use when a large number of vanadium samples were being analyzed
consecutively. In the future, the analyses will be performed in the
Analytical Standards Laboratory using a gas-fusion apparatus whose design
eliminates these problems.

TABLE V-4.   Oxygen Analyses of Vanadium-Wire Detectors
after Equilibration in Sodium at 750°C.

Run No.	Oxygen in Sodium, ppm	Oxygen in Vanadium,[a] wt %
95	0.37	0.444
126	5.04	1.13
128	3.16	0.995, 0.987
130	2.23	0.926
131	5.04	1.140, 1.139
132	0.83	0.638, 0.635
133	0.80	0.608, 0.618
134	2.15	0.865, 0.865
135	2.23	0.877, 0.878
136	5.04	1.12, 1.13
137	10.4	1.40, 1.39
140	0.37	0.443, 0.448
141	0.77	0.577, 0.591
143	5.04	1.11, 1.12
144	10.4	1.40, 1.39
145	15.8	1.59, 1.59
146	4.88	1.10, 1.13

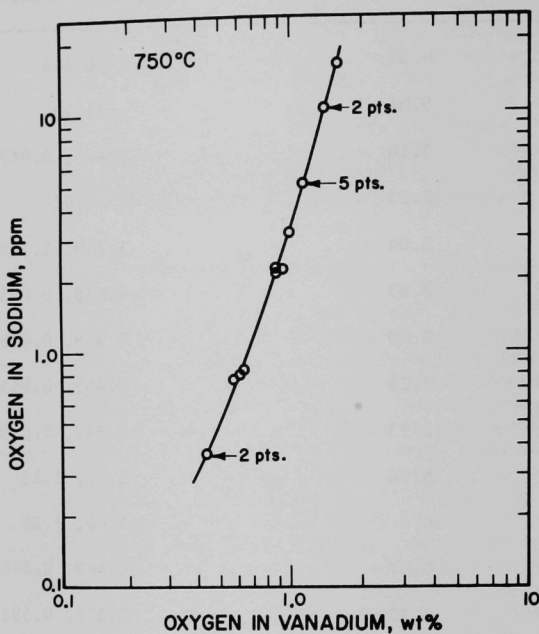[a]Inert-gas fusion analyses performed by ANL Chemistry Division.

Fig. V-1. Equilibrium Distribution of Oxygen Be-
tween Vanadium and Sodium at 750°C.
Neg. No. MSD-54652.

At the request of RDT, a characterization program is being conducted to determine the effect of the nonmetallic impurities carbon, nitrogen, and hydrogen on the measurement of oxygen in sodium by the vanadium-wire equilibration method. No measurable effect on the analysis is expected if vanadium is exposed under the proposed conditions (i.e., 750°C for 4 hr) for the following reasons: (1) The solubility of carbon in vanadium is much less than that of oxygen, and the vanadium typically picks up only several hundred parts per million carbon upon exposure to sodium. (2) Although hydrogen has a very high solubility in vanadium, samples that have been exposed to cold-trapped sodium contain only a few hundred parts per million hydrogen. (3) Compared with the other three nonmetallic elements, nitrogen has such a low diffusivity in vanadium that it is not possible to change the nitrogen concentration in vanadium measurably during a standard 4-hr exposure. From these considerations, one cannot conclude that no interaction occurs between these elements in either vanadium or liquid sodium, over the entire range where mutual solubility occurs in the two phases. One can conclude, however, that it would be difficult to observe such effects under the restricted exposure times and for the low impurity concentrations imposed by cold-trap temperatures of interest in reactor operations.

Even though an investigation of impurity interactions is not within the scope of this work, and accurate measurement or independent control of the concentrations of all four nonmetallic elements in sodium is not within present capability, exploratory experiments are being conducted to determine whether significant interferences in the oxygen analysis can result from atypical sodium-purity conditions.

The effect of carbon is being measured by comparing the oxygen concentration in vanadium wires equilibrated in sodium with and without carbon source in the loop, for otherwise identical conditions. The original distribution-coefficient data for oxygen were obtained under conditions of very low carbon in sodium to minimize any carbon-interaction effects. The results in Table V-5 indicate that changing the carbon concentration in sodium has no effect on the oxygen concentration as determined by the vanadium-wire method at the 0.77 and 4.3 ppm oxygen levels. As was shown in Table V-2 of the preceding section, carbon concentrations in sodium of the order of ∿13 ppm result in ∿1.0 wt % carbon in the austenitic stainless steels at temperatures above 650°C. These carbon concentrations in the steels and in sodium are considerably higher than those expected in operating reactor sodium systems.

Since the diffusivity of nitrogen in vanadium is very low in comparison with that of oxygen, the nitrogen concentration in vanadium will not change during the recommended short exposure to liquid sodium. However, the vanadium wire obtained from various suppliers will vary in nitrogen concentration. To determine whether this will cause any problems with the oxygen analyses, vanadium wire was doped with approximately 450 and 750 ppm nitrogen in a Sievert's apparatus prior to exposure to sodium at two oxygen levels (0.8 and 5 ppm). The results in Table V-6 indicate no measurable effect of the nitrogen additions on the oxygen concentration in vanadium exposed to sodium with 0.8 ppm oxygen. The analyses of the wires from the tests with 5 ppm oxygen in sodium have not been completed.

TABLE V-5. Oxygen Analyses of Vanadium Wires Exposed to
Sodium of Varying Carbon Contents

Test No.	Oxygen in Na, ppm	Oxygen in V, wt %	Carbon in V, ppm	Carbon[a] in Na, ppm	Carbon Source
1	0.77	0.596 0.599	307	0.3 0.6 1.6	No
2	0.77	0.568 0.593 0.555	400 446	7.3 10.6 9.2	Yes
3	4.3	1.06	274	1.2 0.4 2.0	No
4	4.3	1.04 1.07 1.09	355	10.5 14.8 10.4	Yes
5	4.3	1.07 1.07 1.07	488	1.2 2.6	Yes

[a]Analyzed by oxyacidic flux method.

TABLE V-6. Analyses of Simultaneously Equilibrated[a] Vanadium
Wires of Varying Nitrogen Contents

Nitrogen, ppm	Oxygen, wt %
130	0.575
170	0.592
510	0.596
380	0.606
720	0.589
770	0.587

[a]0.80 ppm oxygen in sodium.

An additional test was conducted by simultaneously equilibrating
vanadium wires obtained from different sources in sodium containing 4.9
ppm oxygen. The results given in Table V-7 confirm that nitrogen con-
centrations in vanadium below ~1000 ppm have a negligible effect on the
equilibration method for oxygen analysis of sodium.

TABLE V-7. Oxygen Analyses of Simultaneously Equilibrated[a]
Vanadium Wires Obtained from Various Sources

Wire Batch No.	Nitrogen, ppm	Oxygen, wt %
2	820	1.11
4	230	1.10
	220	1.13
6	110	1.09
	90	1.08

[a]4.9 ppm oxygen in sodium.

The effect of hydrogen on the oxygen analysis is being determined by
adding gaseous hydrogen to a loop that is equipped with a cold trap. Since
the cold trap, which is used for oxygen control, also controls the hydrogen
concentration in sodium, the range of hydrogen levels attainable is limited.
The results obtained in these tests will be compared with the original
distribution-coefficient measurements, which were made when the cold trap
was depleted of hydrogen in order to minimize any effect of hydrogen.

Results of these tests will be reported when all the hydrogen and oxygen analyses of the vanadium wires are available.

Correlation of Results from the Equilibration Method for Oxygen with Emf Measurements. During the development of the vanadium-wire method, the sodium loop in which the data were obtained was equipped with electrochemical oxygen meters as a check on system operation. Because standard Westinghouse meters (see Section I.A) were not available, other types of oxygen meters were used; these included United Nuclear Corporation (UNC) meters of the type

$$Cu, Cu_2O \ || \ ThO_2-15 \ wt \ \% \ Y_2O_3 \ || \ Na, \ \underline{O}_{Na} \tag{I}$$
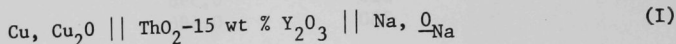
and modified meters of the type

$$Na, Na_2O \ || \ ThO_2-15 \ wt \ \% \ Y_2O_3 \ || \ Na, \ \underline{O}_{Na} \tag{II}$$
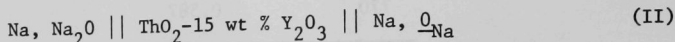
Figure V-2 is a plot of the emf data from a UNC meter (Cell 4) versus the logarithm of oxygen concentration in sodium; oxygen concentrations were determined by the vanadium-wire equilibration method using the distribution-coefficient data reported in the preceding section. The cell was operated at 352°C (625°K) and the vanadium wires were equilibrated under standard conditions, i.e., 4 hr at 750°C. Noteworthy is the fact that the semilogarithmic plot is linear over two orders of magnitude in oxygen concentration, extending to levels below 1 ppm oxygen in sodium.

The operating characteristics of a modified meter of Type II, which has been operated on the same sodium apparatus, have also been investigated. This cell has the same type of electrolyte housing and electrolyte tube as the UNC cell; however, the Cu, Cu_2O electrode has been replaced by 0.5 g of Na to which 25 mg of Na_2O_2 had been added to produce the desired Na, Na_2O electrode. For most of its operating history, this cell has been at a temperature of 352°C (625°F); however, it has also been operated for periods at temperatures of 252, 302, and 402°C. Figure V-3 is a plot of the cell voltage as a function of oxygen concentration in sodium, which was determined from the solubility at the cold-trap temperature using the equation[4]

$$\log C_{\underline{O}(Na)} \ (ppm) = 6.940 - 2801 \ T^{-1}$$

The numbers associated with the data points refer to the order in which the data were taken. The small scatter in the data is attributed to an insufficient period for equilibrium conditions to be established in the loop. In general, the data were obtained at least 24 hr after stable conditions were attained in the loop.

As was the case for the standard UNC meters reported previously,[9] the slope of the experimental curve is significantly greater than the

[8]B. Minushkin, M. Kolodney, UNC-5131 (1967).

[9]Sodium Technology Quarterly Report, October-December, 1970, ANL/ST-8, (1971).
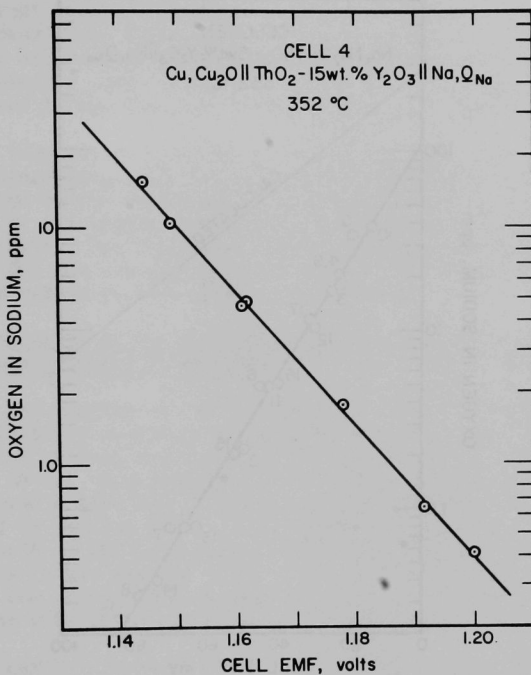
Fig. V-2. Cell Voltage as a Function of Oxygen Concentration in Sodium Measured by the Vanadium-Wire Equilibration Method. Neg. No. MSD-54651.
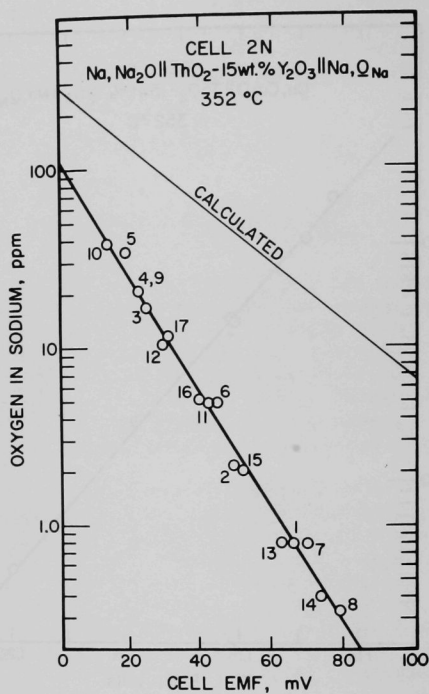
Fig. V-3. Cell Voltage as a Function of Oxygen Concentration in Sodium for an Electrochemical Cell with a Na, Na$_2$O Reference Electrode (325°C). Neg. No. MSD-54482.

curve calculated from available free energy and solubility data on the basis of an ionic transference number of unity for the ThO_2-15 wt % Y_2O_3 electrolyte. The slope of 31 mV/decade for this cell is in good agreement with the values obtained for UNC meters 2 and 4.[9] This semilogarithmic plot is also linear over two orders of magnitude in oxygen concentration and extends to levels below 1 ppm oxygen in sodium. These similar results for two different types of cells suggest that deviations from theoretical predictions result from problems associated with the purity of the thoria-15 wt % yttria electrolyte rather than with the reference electrodes. The electrolyte material used in these cells was not the high-purity material now being tested in the National Meter Program (see Section I.A).

The temperature coefficient of the Na, Na_2O cell was also measured in the temperature range 525 to 675°K at 0.8 ppm oxygen in sodium (Fig. V-4). The slope of the experimental curve approaches that of the calculated curve at the higher temperatures (>600°K) even though the voltages are somewhat lower. The slopes of the temperature-coefficient curves for UNC Cell 2 at 2.1 and 4.9 ppm oxygen in sodium were also in agreement with the calculated values in this temperature range.[9]

2. Application of the Equilibration Method to the Measurement of Carbon Activity in Sodium

The application of the equilibration method to the measurement of carbon activity in sodium is being investigated. Considerations leading to the selection of iron and vanadium as detector metals were given in ANL/ST-8, pp. 59-60. Experiments to determine the equilibrium distribution of carbon between sodium and these metals are being conducted in the sodium loop described in Section V.A.1. Iron foils and vanadium and iron wires are being exposed at 750°C to cold-trapped liquid sodium with and without a carbon source in the system. Results of carbon analyses of the metal specimens and the sodium samples obtained during the runs are given in Table V-8 along with information on the exposure conditions.

The carbon concentration in the vanadium wires were higher when exposed to sodium while (or immediately after) a carbon source was present in the loop (runs 2, 4, 5, 7, 9, and 10). A reduction in the carbon activity in the sodium after removal of the carbon source is indicated by the carbon analyses of the vanadium wires from runs 3, 6, and 8. In general, the carbon analyses of the sodium samples and the vanadium wires are in qualitative agreement, i.e., both indicate the same trend upon increasing and decreasing the carbon activity in the sodium.

The results for the iron are difficult to interpret because most of the carbon values are in the range of 20 to 30 ppm and do not increase or decrease as expected when a carbon source is either inserted or removed from the loop. Carbon contents in the iron were expected to range from ∿5 to 30 ppm, depending on the carbon content of the sodium.

Three potential problems in the use of iron as a detector are being investigated. First, the high diffusivity of carbon in iron can result in a redistribution of the carbon between sodium and iron during cooling of the specimens. Only 10 min is required to equilibrate a 0.37-mm
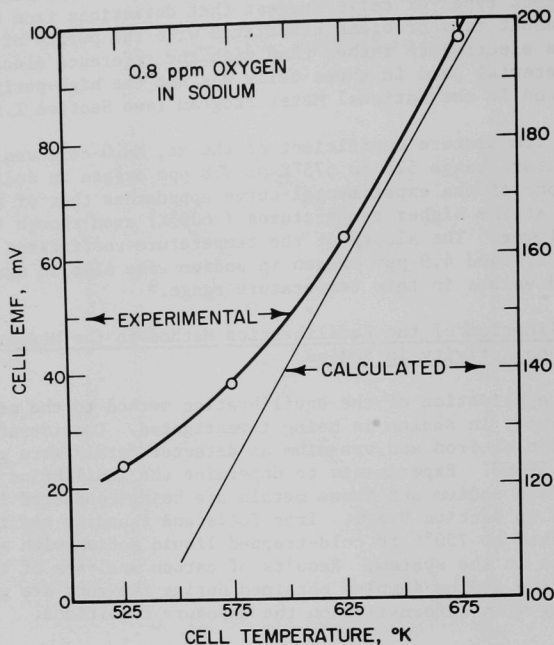
Fig. V-4. Comparison of Experimental and
Calculated Temperature Coeffi-
cients of an Electrochemical
Cell with a Na, Na₂O Reference
Electrode. Neg. No. MSD-54480.

TABLE V-8. Carbon Analyses of Sodium and Vanadium and Iron Detectors after 750°C Exposures to Cold-Trapped Sodium

| Run No. | Carbon Concentration (ppm) in | | | Sodium Conditions |
	Vanadium	Iron	Sodium	
1	168, 178	–	0.7, 0.4	No carbon source
2	357, 347	–	–	Carburized Fe-8 Ni source
3	195, 191	30.3, 30.8	–	24 hr after carbon source was removed.
4	234, 236	27.4, 22.2	5.3, 2.6, 3.7	Carburized Fe-8 Ni source
5	394	21.4, 22.5	1.5, 0.9, 1.1	96 hr after carburized Fe source was removed
6	307	20.7, 15.5, 19.5	0.6, 0.6, 0.8 0.3, 0.6, 1.6	640 hr after carbon source was removed
7	400, 446	22.5, 21.0	7.3, 10.6, 9.2	Carburized Fe source
8	274	25.0, 15.6	1.2, 0.4, 2.0	No carbon source
9	355	16.2, 9.6	10.5, 14.8, 10.4	1 hr after carbon source was removed
10	488	11.0, 10.8	1.2, 2.6	24 hr after carbon source was removed

diameter wire at 750°C; therefore, rapid cooling rates are required to retain the equilibrium carbon concentration. Samples with larger cross sections are being used in an attempt to evaluate and eliminate this problem.

Secondly, possible chromium transport and deposition on the iron may lead to the formation of chromium carbide, which could account for the erratic carbon contents. Thin surface layers of the iron wires will be removed by chemical etching prior to the carbon determinations in an attempt to determine whether this is a problem.

Thirdly, the effect of low concentrations of carbide-forming impurities (e.g., Si, Cr, and Mn) in the Armco iron must be considered in these experiments. Internal carburization of approximately 100 ppm (total) of these elements could account for ~10 ppm carbon in the iron upon exposure to sodium with a very low carbon activity. To examine this possibility, the Armco iron previously used and higher-purity iron will be equilibrated simultaneously in sodium.

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